Heteroleptic Co(III) bisdithiocarbamato-dithione complexes: Synthesis, structure and bonding of [Co(Et₂dtc)₂(R₂pipdt)]BF₄ (R = Me, 1; Ph, 2; pipdt = piperazin-2,3-dithione) complexes

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ABSTRACT
The reaction between the binuclear cobalt complex, [Co₂(Et₂dtc)₅], and Me₂pipdt and Ph₂pipdt ligands has provided almost quantitatively the cobalt tris-chelate heteroleptic complexes [Co(Et₂dtc)₂(R₂pipdt)]BF₄ (1 and 2). The molecular structure of 2 shows the metal in a distorted octahedral geometry. The nature of the bonding in these complexes has been elucidated with the support of DFT TD-DFT calculations. Both chelating S,S donors work as weak-field ligands. The comparison of the chemical reactivity for the homoleptic dithiocarbamate complex [Co(Et₂dtc)₃] and the heteroleptic [Co(Et₂dtc)₂(Ph₂pipdt)]⁺ derivative shows that the global softness σ is significantly higher in [Co(Et₂dtc)₂(Ph₂pipdt)]⁺ than in the homoleptic dithiocarbamate complex, due to a reduction of nephelauxetic effect induced by the dithioxamide ligand. The kinetics for the reaction between the reagents in CH₂Cl₂ has been followed spectrophotometrically as a function of temperature in pseudo-first order conditions with respect to R₂pipdt ligands. Kinetic results further support a reaction mechanism involving a one-end reversible dissociation of the [Co₂(Et₂dtc)₅]⁺ dimer forming a reactive cobalt(III)dithiocarbamate center susceptible to attack by nucleophiles. The effectiveness and versatility of the above reaction is an easy and clean method to provide heteroleptic-dithiocarbamates with a variety of suitable ligands of interest for applicative purposes.

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Dedicated to Professor Giovanni De Munno for celebrating his seminal contribution to Coordination Chemistry

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1. Introduction

Transition metal-dithiocarbamates (dithiocarbamato = R₂dtc) represent a well-known class of complexes exhibiting a variety of structural, bio-medical, environmental, optical and magnetic properties [1–6]. Moreover, these complexes, in addition to their intrinsic interest, are suitable starting precursors, valuable also for their relatively low cost and easy preparation, to produce metal sulfides that are employed as nanocrystals for several high-tech applications [7].

In heteroleptic cobalt dithiocarbamate complexes the presence of one or more different ligands may improve the above-mentioned properties. For example, complexes where one dtc ligand is substituted by two monodentate or one bidentate donor such as py = pyridine or bidentate nitrogen mustards have shown biological activities [8]. In most of the cited cases, the synthetic procedure includes a two-step reaction, one of the mono or bidentate donor with the hydrated cobalt(II) chloride followed by a displacement reaction of halogens with the dithiocarbamate ligands. To the best of our knowledge, no structural characterization of the obtained products supposed to be Co(II) complexes is available. Similarly in some instances homoleptic cobalt(II) dithiocarbamates [9] are invoked despite these complexes being extremely oxygen sensitive and in organic solvents rapidly oxidize in air even in the presence of reducing agents [7a, 10]. A very effective procedure for the synthesis of heteroleptic cobalt dithiocarbamate complexes by reacting dimeric cobalt(III) dithiocarbamate complexes [Co₂(R₂dtc)₃]⁺ with selected ligands has been proposed since 1975 [11]. Through this method, cobalt(III)bis(dithiocarbamato)-ethylenediamines [12] and –dithioxamide and –dithiomalonamide [13] cationic complexes as well as the related kinetic study have been reported. Later, a series of heteroleptic Co(III) dithiocarbamato complexes containing imidazole, amine and pyridine donors, including the structural characterization of a cobalt(III)bis(dithiocarbamato) histamine complex, were obtained [14].
The renewed interest towards heteroleptic cobalt dithiocarbamate complexes prompted us to revisit the above cited reaction by employing disubstituted-piperazin-2,3-dithione (R₂pipdt; R = Me, Ph) as incoming ligands. Both R₂dtc⁻ and R₂pipdt can work as coordinating chelating S,S donors (R₂dtc⁻ is negatively charged) with a possible thioureide contribution to their resonance forms, as shown in Chart 1.

As cited above, R₂dtc⁻ could coordinate most metals and may stabilize metal centers in low oxidation states as a strong-field ligand (Chart 1, A) or in high-oxidation state as a weak-field ligand (Chart 1, B and C). This occurs with cobalt which adopts a low-spin d⁶ electronic configuration and octahedral geometry in [Co(R₂dtc)₃]. These complexes are inert and stable [7a, 10, 15]. Also dithioxamide ligands can work as S,S-chelating ligands to a metal, behaving as weak-field ligands (Chart 1, II, III, IV). In metal complexes planarity inside the thioamide system is generally preserved, while planarity inside the M(S₂C₂) pentatomic ring is rarely observed with the acyclic dithioxamides, different to what happens with R₂pipdt ligands [16]. Reaching planarity allows these ligands, for example when coordinated in a square-planar coordination to Ni(II), to be assigned as the fully oxidized form of dithiolene ligands, a class of redox-active ligands capable to undergo reversible redox processes from the dianionic to the neutral form [17]. These ligands have been used to synthesize Ni-triad both homoleptic and heteroleptic (R₂pipdt-dithiolato) complexes. The latter are of interest as second order nonlinear optical chromophores, and the electron-donating/withdrawing features of the ligands, the π-delocalization between them and the nd-metal orbitals have been investigated [18]. The coordinating ability of these ligands combined with the oxidation action of diiodine has been successfully employed to dissolve in mild conditions, even noble-metals [19]. Through this method [Co(Me₂pipdt)₃]₂[I₂]₂(THF)₂ (R = Me) has been obtained and characterized. In this salt the [Co(R₂pipdt)₃]³⁺ (R = Me) cation exhibits octahedral geometry and a low-spin d⁶ electronic configuration [20].

Here [Co(Et₂dtc)₂R₂pipdt]BF₄ (R = Me, 1; Ph, 2), including the crystal structure of 2, is presented with the goal to elucidate, with the support of DFT calculations, the nature of the bonding in these complexes, and to point out once more the versatility of the substitution reaction, also with the support of kinetic results, on the binuclear cobalt complex [Co₂(R₂dtc)₃]³⁺ to easily provide heteroleptic cobalt dithiocarbamato complexes: [Co(R₂dtc)₂LL]^x (x depending on the LL charge), which may be useful for a variety of applications.

2. Experimental

Reagents and solvents of reagent grade and spectroscopic grade have been used as received from Sigma-Aldrich. Elemental analysis was performed by a Carlo Erba CHN Elemental Analyzer model EA1108. FT-IR spectra were recorded on KBr pellets from
400–4000 cm\(^{-1}\) with a Bruker Equinox 55 spectrophotometer. UV-visible absorption measurements were performed with an Agilent Cary500 UV-Vis-NIR spectrophotometer.

### 2.1. Synthesis

The ligands, N,N-dimethyl-piperazine-2,3-dithione (Me\(_2\)pipdt), N,N-diphenyl-piperazine-2,3-dithione (Ph\(_2\)pipdt), and the complex, [Co\(_2\)(Et\(_2\)dtc)\(_5\)]BF\(_4\), were synthesized according to references [21] and [11], respectively.

\[ [\text{Co(Et}_2\text{dtc)}_2(R_2\text{pipdt})]\text{BF}_4 \quad (R = \text{Me (1)}; R = \text{Ph (2)}) \]

Approximately equimolecular amounts of the reactants, [Co\(_2\)(Et\(_2\)dtc)\(_5\)]BF\(_4\) 1.00 g (1.06·10\(^{-3}\) mol) and R\(_2\)pipdt 0.19 g (1.09·10\(^{-3}\) mol) R = Me, and 0.32 g (1.07·10\(^{-3}\) mol) R = Ph, were allowed to react in CH\(_2\)Cl\(_2\) for one hour under reflux according to Scheme 1. The solvent was evaporated to dryness and the crude product, extracted with minimum ethanol, left a green solid (characterized as [Co(Et\(_2\)dtc)\(_3\)]). Brown solids of 1 (0.63 g, 96%) and 2 (0.74 g, 94%) were obtained in high yields by addition of petroleum ether to the ethanolic solution. These solids were recrystallized from CH\(_2\)Cl\(_2\)/petroleum ether 60–80\(^\circ\)C. Well-formed crystals of 2, suitable for X-ray crystallographic studies, were obtained by slow diffusion of Et\(_2\)O in CH\(_3\)CN solutions. Elemental analysis CHN 1. Calcd. for CoC\(_{16}\)H\(_{30}\)N\(_4\)S\(_6\)BF\(_4\) (%): C% 31.17; H% 4.90; N% 9.09. Found. C% 31.56; H% 5.04; N% 8.83. 2. Calcd. for CoC\(_{26}\)H\(_{34}\)N\(_4\)S\(_6\)BF\(_4\) (%): C% 42.16; H% 4.69; N% 7.68. Found. C% 42.30; H% 5.03; N% 7.56. FT–IR (KBr): \(\nu_{\text{max}}\) (cm\(^{-1}\)) 1: 2976m, 2931m, 1541s, 1457m, 1438m, 1407w, 1360s, 1279s, 1209m, 1147s, 1083s, 914w, 853w, 782w, 532–522vw; 2: 2976m, 2927m, 2853w, 1540w, 1507vs, 1456w, 1438m, 1358s, 1277s, 1208m, 1148m, 1124m, 1084vs, 1037m, 1002w, 852w, 763w, 696w, 668w, 624w, 553–533w; UV-vis \(\lambda_{\text{max}}\) (nm), \(\varepsilon\) (cm\(^{-1}\) mol\(^{-1}\) L): 1. 602, 2300; 2. 663, 1820.

### 2.2. X-ray crystallography

Single crystal data for 2 were collected with a Bruker Smart 1000 area detector diffractometer (Mo K\(\alpha\); \(\lambda = 0.71073\) Å). Data collection was performed with a 0.3° scan and with several series of exposure frames covering at least a hemisphere of the reciprocal space [22]. A multiscan absorption correction was applied to the data using SADABS [23]. The structures were solved by direct methods (SIR programs) [24] and refined with full-matrix least-squares (SHELXL) [25] using the Olex2 software package [26]. All non-H atoms were refined with anisotropic displacement parameters. The BF\(_4\)\(^-\) anion was modelled over three distinct sites (with 0.45/0.35/0.20 site occupancy factors). CCDC 2174262 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).
2.3. Computational details

Computational studies on the ground-state electronic structure of \([\text{Co}((\text{Et}_2\text{dtc})_2(\text{Ph}_2\text{pipdt}))^+]\) and \([\text{Co}((\text{Et}_2\text{dtc})_3)]\) in both the gas phase and \(\text{CH}_2\text{Cl}_2\) solution were performed at DFT [27] level employing the GAUSSIAN 16 [28] software package. The Becke three-parameter exchange functional with Lee–Yang–Parr correlation functional (B3LYP) [29, 30] was used. The ground state geometries were obtained by full geometry optimization without any symmetry constraints; moreover, the absence of negative frequencies confirmed that the stationary points correspond to minima on the potential energy surfaces. The basis sets employed were 6-31\(^+\)G\(^\ast\)/C\(^3\)/C\(^3\)/[31] (for C, H, N and S) and LANL2DZ [32] (for cobalt). All structures for the optimization were input starting from the crystallographic data. The effects of solvation were considered by the Polarizable Continuum Model (PCM) using a \(\text{CH}_2\text{Cl}_2\) simulated electric field (\(\varepsilon = 8.93\)). The 30 lowest singlet excited states of the closed shell complexes were calculated within the time-dependent DFT (TD-DFT) formalism as implemented in Gaussian [33, 34], both in the gas phase and in \(\text{CH}_2\text{Cl}_2\). The depictions of optimized molecular structures and orbital isosurfaces were obtained using ArgusLab 4.0 [35].

2.4. Kinetic experiments

For kinetic experiments, a multicell temperature-controlled system was used and experiments were set up using the Scanning Kinetics software. The two reactants were first introduced separately in a double chamber quartz cuvette and successively mixed at \(t = 0\).
3. Results and discussion

3.1. Synthesis, structural and spectroscopic studies

[Co(III)(Et2dtc)2R2pipdt]BF4, 1 and 2 have been obtained according to Scheme 1.

As detailed in the Experimental section, the crude products were collected as solids for solvent evaporation. [Co(Et2dtc)2R2pipdt]BF4 was dissolved by treatment of the solid with ethanol, and [Co(Et2dtc)3] recovered as undissolved green fraction. The [Co(Et2dtc)2R2pipdt]BF4 [R = Me (1), R = Ph (2)] salts have been obtained in almost quantitative yield by addition of petroleum ether and recrystallization by slow diffusion of Et2O in CH3CN solutions. Well-formed crystals of [Co(Et2dtc)2Ph2pipdt]BF4 (2) were obtained and characterized by X-ray diffraction studies. A summary of data collection and structure refinement is reported in Table 1. The molecular structure of 2 is displayed in Figure 1, and selected bond lengths (Å) and angles (°) are reported in Table 2.

Compound 2 is characterized by the presence of a cationic cobalt(III) complex and a BF4⁻ anion. The metal center exhibits distorted octahedral geometry achieved by coordination of two S,S bidentate anionic Et₂dtc ligands, one S,S bidentate neutral Ph₂pipdt. Given the presence of three bidentate ligands connected to the metal center, the complex molecule is chiral with both Δ and Λ enantiomers present (centrosymmetric space group P2₁/c). In agreement with the general behavior observed for the R₂pipdt ligand class (R = Me, Bz, i-Pr), the C–C bond distance (1.50(1) Å) between

![Figure 1. Molecular structure of 2. Thermal ellipsoids are reported at the 30% probability level.](image)

**Table 2. Selected bond lengths (Å) for 2.**

| Bond  | Length (Å) |
|-------|------------|
| Co-S₁₁ | 2.218(2)   |
| Co-S₁₂ | 2.209(2)   |
| Co-S₁₃ | 2.275(2)   |
| Co-S₂₁ | 2.277(2)   |
| Co-S₂₂ | 2.255(3)   |
| Co-S₂₃ | 2.268(3)   |
| C₁₁–C₂₁ | 1.50(1)   |
| C₁₁–N₂₁ | 1.308(9)  |
| C₁₁–N₁₂ | 1.312(9)  |

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the thioamido groups of Ph₂pipdt is indicative of single bond character (see Chart 1). The torsion angle S-C-C-S of Ph₂pipdt is approximately 17° and the deviation from planarity is ascribable to the C-C single bond character previously mentioned and the flexibility of the ethylene moiety. By inspecting the geometric parameters pertaining to the coordination environment, it can be appreciated how the Co-Spipdt bond distances (2.209(2) and 2.218(2) Å) are significantly shorter than those of the dithiocarbamate moieties Co-Sdtc (2.255(3)-2.277(2) Å range). Similarly, C-Spipdt bond distances (1.671(8) and 1.690(8) Å) are significantly shorter than those of the dithiocarbamate moieties C-Sdtc (1.705(9)-1.717(8) Å range), pointing to a more pronounced C-S single bond character for the Et₂dtc ligands with respect to the thione moieties in Ph₂pipdt. Overall, from a survey on the CCDC, there is a substantial agreement between the behavior of the two ligands in 2 with the geometric parameters found in heteroleptic [Co(dtc)₂L] or homoleptic [Co(dtc)₃] complexes (L = bidentate ligand) [20].

Optimized molecular structures in gas phase and in CH₂Cl₂ calculated by DFT methods are reported in Figure S2. Structural findings agree with vibrational spectroscopy results (see Figure S1) where the decrease of CN distances relatable to an increase of the contribution of the resonance forms II and III to the thioamide-like moieties of R₂pipdt (Chart 1) is reflected by a shift of related vibration on coordination. Accordingly, the ν(CN) stretching vibrations of R₂pipdt free ligands, 1503 cm⁻¹, R = Me; 1489 cm⁻¹, R = Ph, are shifted, respectively, to 1541 cm⁻¹ and 1540 cm⁻¹ in 1 and 2 (Figure S1). Similarly, a shift to higher frequency for ν(CN) of Et₂dtc on going from the homoleptic [Co(Et₂dtc)₃] (1492 cm⁻¹) to the heteroleptic complexes (1507 cm⁻¹ and 1510 cm⁻¹ for 1 and 2, respectively) reflects an increase of the contribution of the resonance form B to the thioamide-like nature of Et₂dtc (Chart 1) in agreement with their weak-field ligand character.

DFT calculations based on the GAUSSIAN 16 [28] software package have been performed both in vacuum and in CH₂Cl₂ solutions for [Co(Et₂dtc)₂(Ph₂pipdt)]⁺ as detailed
in Experimental and in Supplementary Information. A satisfactory agreement between experimental and calculated bond lengths is obtained (see Table S1) by taking into account the absence of crystal packing forces on the molecules in these phases. Molecular orbitals obtained thereof are reported in Figure 2. As shown, the HOMO is located mainly on the two Et2dtc ligands, p-orbitals of one S atom with a small N contribution while the LUMO is located on the Ph2pipdt ligand through the p orbitals of the S2C2N2 moiety in $\pi^*$ combination. The d orbitals contribution becomes relevant from the HOMO-1 downwards in energy, as well as in the LUMO + 1 and LUMO + 2 (in $\pi^*$ interaction with the p-sulfur atoms of the ligands). The energy gap between HOMO and LUMO is 2.971 eV.

TD-DFT calculations are summarized in Tables S1–S3 and are useful in assigning the observed absorption spectra. Figure 3 reports the absorption spectrum of [Co(Et2dtc)2(Ph2pipdt)]$^+$ (blue) compared to the simulated one retrieved from TD-DFT calculations (grey). The electronic spectra of 1 and 2 in CH2Cl2 solutions are characterized by strong absorption in the UV-Vis region which extends to approximately 500 nm and medium intense bands in the visible region: (602(1), 665(2)) nm and a shoulder at 470 nm for 2. According to TD-DFT calculations, the two lowest energy bands are associated to transitions that involve a relevant contribution of the metal d-orbitals and of p-orbitals of the sulfur atoms of the ligands (Figures S3, S4, and Table S4). In particular, the lowest energy band at 665 nm (21276.6 cm$^{-1}$) consists of transitions mainly from HOMO-3, HOMO-4 and HOMO-5 which contain the contribution of the metal $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals, respectively, to the LUMO + 1 and LUMO + 2 associated to the $d_{x^2-y^2}$ and $d_{z^2}$ metal orbitals. The second lowest energy band at 470 nm (15037.6 cm$^{-1}$) has similar contributions and additionally involves the HOMO-2 and HOMO-1 orbitals for the starting state of the transition, corresponding to the $d_{xz}$...
and $d_{yz}$ metal orbitals (with a more relevant contribution of the ligand $p$ orbitals on sulfur atoms). In a simplified ligand-field configuration for octahedral $d^6$ Co$^{3+}$ complexes, by associating the lowest energy bands to the spin permitted transitions $^1A_{1g} \rightarrow ^1T_{1g}$ (665 nm) and $^1A_{1g} \rightarrow ^1T_{2g}$ (470 nm) (Figure 3), it is possible to estimate the $\Delta_D$ as 16406 cm$^{-1}$ (2.03 eV) with a Racah parameter $B = 469$ cm$^{-1}$. The calculated nephelauxetic parameter $b$, corresponding to the ratio between the experimental $B$ value for the complex and the $B$ value referred to a free Co$^{3+}$ ion (1065 cm$^{-1}$), has a value of 0.440. This parameter represents the strength of the interelectronic repulsion, and the low value indicates that the electron cloud is relatively delocalized in the complex. This observation explains the low spin configuration of Co$^{3+}$ in 
\[ \begin{align*} \text{[Co(Et_2dtc)_2(Ph_2pipdt)]}^+ \end{align*} \]
despite the relatively low $\Delta_D$ splitting. This is in agreement with the significant contribution of ligands orbitals to the frontier MOs. Similar results are obtained for the homoleptic 
\[ \begin{align*} \text{[Co(Et_2dtc)_3]} \end{align*} \]
complex, which yields the following values: $\Delta_D = 16632$ cm$^{-1}$; $B = 336$ cm$^{-1}$ and $b = 0.315$. By comparison, it can be concluded that the introduction of the cyclic dithioxamide significantly weakens the nephelauxetic effect with respect to the homoleptic tris-chelated dithiocarbamate complex, while negligibly affecting the $\Delta_D$ splitting. The observed difference in the absorption profile of the two compounds, in regard to the position and intensity of the lowest energy bands, is therefore mainly governed by electron delocalization rather than crystal field effects.

The chemical reactivity descriptors retrieved from DFT-calculated energy values of the HOMO and LUMO orbitals for the homoleptic dithiocarbamate complex [Co(Et$_2$dtc)$_3$] and the substituted [Co(Et$_2$dtc)$_2$(Ph$_2$pipdt)]$^+$ derivative are reported in Table 3. The global softness $\sigma$, which represents the tendency of the electron cloud to be distorted under external perturbation, is significantly higher in [Co(Et$_2$dtc)$_2$(Ph$_2$pipdt)]$^+$ than in the homoleptic dithiocarbamate complex, thus confirming the previous observation that the dithioxamide ligand induces a reduction of nephelauxetic effect and therefore a more extended charge delocalization. The remarkable difference in the electrophilicity index $\omega$ values further confirms this conclusion, underlining the increased capability of the cationic heteroleptic [Co(Et$_2$dtc)$_2$(Ph$_2$pipdt)]$^+$ complex to accommodate an extra charge with respect to the dithiocarbamate homoleptic precursor.

| Table 3. Chemical reactivity descriptors (eV). |
|-----------------------------------------------|
|                                      | 2         | [Co(Et$_2$dtc)$_3$] |
|-----------------------------------------------|
| Chemical potential $\mu = \frac{E_{\text{HOMO}} + E_{\text{LUMO}}}{2}$ | $-7.091$ | $-3.688$ |
| Global hardness $\eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2}$ | $1.296$ | $1.944$ |
| Global softness $\sigma = \frac{1}{2\eta}$ | $0.386$ | $0.257$ |
| Electrophilicity index $\omega = \frac{\mu^2}{2\eta}$ | $19.399$ | $3.498$ |
| Electronegativity $\chi = \frac{1}{\mu}$ | $7.091$ | $3.688$ |
| Ionization potential $I = -E_{\text{HOMO}}$ | $8.386$ | $5.682$ |
| Electron affinity $A = -E_{\text{LUMO}}$ | $5.795$ | $1.694$ |

and Co$^{3+}$ complexes, by associating the lowest energy bands to the spin permitted transitions $^1A_{1g} \rightarrow ^1T_{1g}$ (665 nm) and $^1A_{1g} \rightarrow ^1T_{2g}$ (470 nm) (Figure 3), it is possible to estimate the $\Delta_D$ as 16406 cm$^{-1}$ (2.03 eV) with a Racah parameter $B = 469$ cm$^{-1}$. The calculated nephelauxetic parameter $b$, corresponding to the ratio between the experimental $B$ value for the complex and the $B$ value referred to a free Co$^{3+}$ ion (1065 cm$^{-1}$), has a value of 0.440. This parameter represents the strength of the interelectronic repulsion, and the low value indicates that the electron cloud is relatively delocalized in the complex. This observation explains the low spin configuration of Co$^{3+}$ in 
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3.2. Kinetics

The reaction between the binuclear cobalt complex \([\text{Co}_2(\text{Et}_2\text{dtc})_5]^+\) and \(\text{Me}_2\text{pipdt}\) and \(\text{Ph}_2\text{pipdt}\) ligands has been followed by spectrophotometric measurements by monitoring, at the chosen temperature, the changes in absorbance of a \(\text{CH}_2\text{Cl}_2\) solution obtained by mixing the complex and ligand in excess under pseudo-first order conditions. By plotting \(\ln(A_\infty - A_t)\), at a convenient wavelength at which \((\Sigma_{\text{products}} - \Sigma_{\text{reagents}})\) is large, against time, straight lines with slopes corresponding to the observed rate constants, \(k_{\text{obs}}\), have been obtained. By plotting the \(k_{\text{obs}}\) values versus \(\text{R}_2\text{pipdt}\) concentrations, a two-term rate law: 

\[
k_{\text{obs}} = k_{\text{I}} + k_{\text{II}}/C_1[\text{R}_2\text{pipdt}]
\]

is found (Figure 4a and b). The obtained values of \(k_{\text{II}}\) (slope), where \(k_{\text{II}} \gg k_{\text{I}}\), are listed in Table 4. The \(k_{\text{I}}\) values are affected by a large error since they provide a small contribution to \(k_{\text{obs}}\). Activation enthalpy \((\Delta H^\#)\) and entropy, \((\Delta S^\#)\), have been calculated from experimental \(k_{\text{II}}\) values from the Eyring’s equation as described in SI (Figure 4c); the relatively large errors associated to the rate constants also affect activation parameter values.

When acyclic dithiooxamides \([13b]\) or dithiomalonamides (dimorpholyldithiomalonamide = \(\text{Hmodtm}\)) \([13c]\) as incoming ligands were used, the same kinetic behavior was observed. For comparison reasons the related \(k_{\text{I}}\) values and the available activation parameters are reported in Table 5. The higher \(k_{\text{I}}\) value with dithioxamides is observed for \(\text{Ph}_2\text{pipdt}\), possibly due to a higher electron-donation of the Ph group compared with alkyl ones. A modest change of \(k_{\text{I}}\) values when employing cyclic dithiooxamides in place of acyclic ones, or in place of dithiomalonamides where a \(\text{CH}_2\) group is inserted between the two thioamide moieties \([13c]\), is observed, suggesting a small variation of the sulfur nucleophilicity. The closure of the
chelating ring does not affect the reaction rate, as this is a fast process because it does not require further collision between the reagents. A modest change of the available activation parameters, albeit affected by large errors, seems to reflect a similar nucleophilic substitution reaction with small changes of the electronic and steric effect of the investigated incoming ligands (Table 5). Instead the rate constants $k_{II}$ are significantly smaller (approximately ten times) when compared to the values determined by using ethylenediamines [12b]. These results agree with the earlier proposed reaction mechanism depicted in Scheme 2, where S is the solvent and L-L is the cyclic dithioxamide ligand R$_2$pipdt (R = Me, Ph).

This reaction mechanism involves a fast equilibrium preceding the rate-determining step between $[\text{Co}_2(\text{Et}_3\text{dtc})_5]^+$ and an intermediate where $[\text{Co}(\text{Et}_2\text{dtc})_3]$ is one-end linked to a $[\text{Co}(\text{Et}_3\text{dtc})_2]^+$ unit. This intermediate then undergoes the displacement of $[\text{Co}(\text{Et}_2\text{dtc})_3]$ by solvent followed by fast entry of L-L (path a with reaction rate $k_a$) and a bimolecular attack from the nucleophilic ligand (path b with reaction rate $k_b$). The second-order contribution to the rate law is relatable to the nucleophilic participation of L-L, while the apparently first-order one is also related to a bimolecular process in which $[\text{Co}(\text{Et}_2\text{dtc})_3]$ one-end linked is displaced by the solvent, and the process is followed by the fast entry of L-L, in turn displacing the solvent, as supported by experiments performed in more coordinating solvents [12b]. By applying the steady state approximation, assuming that the intermediate is at low concentration, the expression for the pseudo-first order kinetics $k = (k_1/k_2)k_0[S] + (k_1/k_2)k_0[L-L]$, and for $k = k_{obs}$; $(k_1/k_2)k_0[S] = k_1$ and $(k_1/k_2)k_0 = k_{II}$ can be obtained (see Supplemental Material for details). According to the proposed mechanism an associative step should contribute to $k_1$ and $k_{II}$. Activation parameters obtained for $k_{II}$ seem to further support a prevailing associative step contributing to path b of Scheme 2. We note that the products are stable in solution during kinetic experiments and also after several hours at $t = \infty$. Similarly, the solid state crystalline samples, which have been isolated as neutral compounds or salts, do not show any degradation over a 12 month time period. More sophisticated studies, including those based on quantum chemical modes, out of the scope of the present paper, should allow a more detailed description of the above reaction [36].

**Table 5.** Comparison of $10^2 k_{II}$ (mol$^{-1}$ L sec$^{-1}$) determined at 25 °C.$^{a,b}$

|          | Me$_2$pipdt | Ph$_2$pipdt | Et$_2$dto | N,N'Furdto | N,N'Modto | N,N'Pridto | Hmodtm |
|----------|-------------|-------------|-----------|------------|-----------|------------|--------|
| $k_{II}$ | 1.3         | 2.6         | 1.8       | 1.2        | 1.2       | 1.4        | 2.9    |

$^a$Et$_2$dto = N,N,N'-tetraethyl-; N,N'Furdto = N,N'-difurfuryl-; N,N'Modto = N,N'-dimorpholyldithiooxamide; Hmodtm = dimorpholyldithiomalonamide.

$^b$ΔH$^o$ (KJ mol$^{-1}$), ΔS$^o$ (J mol$^{-1}$ K$^{-1}$) = 71 ± 3, -42 ± 8 (N,N'Pridto); 63 ± 4, -59 ± 10 (Hmodtm).

**Scheme 2.** Proposed reaction mechanism. S and L-L represent the solvent and the cyclic dithioxamide ligand R$_2$pipdt (R = Me, Ph), respectively.
4. Conclusion

The heteroleptic cobalt(III) diethyldithiocarbamate-disubstituted-piperazin-2,3-dithione complexes, [Co(Et₂dtc)₂(R₂pipdt)]BF₄ (R₂pipdt = piperazin-2,3-dithione; R = Me, 1; Ph, 2), have been prepared in almost quantitative yields through a substitution reaction on the binuclear cobalt complex [Co₂(Et₂dtc)₅]⁺. The molecular structure of 2, determined through single crystal X-ray diffraction, shows the metal in a distorted octahedral geometry achieved by coordination of two S,S bidentate anionic Et₂dtc ligands and one S,S bidentate neutral Ph₂pipdt, while the charge is balanced by a BF₄⁻ anion. Bond distances in the NCS moieties are in agreement with electron-delocalization inside the thioamide moieties for both ligands. DFT and TD-DFT calculations are useful in describing the bonding, and to assign the observed uv-visible absorptions in these complexes. Kinetic experiments further support that the [Co₂(Et₂dtc)₅]⁺ dimer is an optimal source of a reactive cobalt(III)dithiocarbamato center susceptible to attack by nucleophiles to produce quantitatively heteroleptic complexes. Beyond the intrinsic interest for basic chemistry of the described results related to 1 and 2, it is relevant to underline the effectiveness and versatility of the employed synthetic procedures. We provide to researchers of different backgrounds an easy and clean method to obtain heteroleptic-dithiocarbamate complexes, which may have applications.

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