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Molecular structure and spectroscopic properties of $[Co(Me_2dtc)_2 {(Ph_2PO)_2BF_2}]$ (Me_2dtc = *N*,*N*-dimethyldithiocarbamate)

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Oxidation of a blue ethanolic mixture containing $Co(BF_4)_2 \cdot GH_2O$ and $PCIPh_2$ by tetramethylthiuram disulfide afforded a red-colored complex having a *cis*- $[Co^{III}(Me_2dtc)_2(\mathbf{P})_2]$ environment ($Me_2dtc^- = N,N-dimethyldithiocarbamate$), although the yield was relatively low. Single-crystal X-ray crystallography revealed that the product was $[Co(Me_2dtc)_2(\{Ph_2PO\}_2BF_2\}]$ (**1**), where bis(diphenylphosphinito)difluor-oborate was probably formed by hydrolysis of PCIPh₂ followed by reaction with BF_4^- in ethanol. The same complex was also prepared by hydrolysis of *cis*- $[Co(Me_2dtc)_2(PHPh_2)_2]BF_4$ in a mixture of acetonitrile, methanol and water. The molecular structure and spectroscopic properties of complex **1** were compared with those of the corresponding Ph₂POMe complex, *cis*- $[Co(Me_2dtc)_2(Ph_2POMe)_2]BF_4$.

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1. Introduction

N,*N*-Dimethyldithiocarbamate (Me_2dtc^{-}) [1] is a versatile auxiliary ligand for syntheses of cobalt(III) complexes containing various P-donor ligands (**P**), $[Co(Me_2dtc)_2(\mathbf{P})_2]^+$, owing to its steric compactness and $\sigma\text{-}$ and $\pi\text{-}\text{electron}$ donating properties which make the Co^{III} center softer for better bonding with soft P-donors [2]. In previous studies, we have succeeded in synthesizing and characterizing such complexes bearing a number of monodentate and bidentate P-donor ligands [2-8]. Particularly interesting examples are the complexes with diphenylphosphine (PHPh₂), *cis*- and *trans*- $[Co(Me_2dtc)_2(PHPh_2)_2]BF_4$ [3], because Werner-type cobalt(III) coordination compounds with PHPh₂ are limited [9], presumably due to a very weak σ -donicity of PHPh₂. In this study, we have attempted to prepare analogous complexes with chlorodiphenylphosphine (PClPh₂) having a much weaker σ -donicity and a larger steric demand than PHPh₂ [10]. To our best knowledge the only one precedent example of cobalt(III) compound with PCIPh₂ is $[CpCo{S_2C_2(CN)_2}(PClPh_2)]$ (Cp = $\eta^5 - C_5H_5^-$) [11].

A similar reaction with PClPh₂ to that for *cis*- $[Co(Me_2dtc)_2$ (PHPh₂)₂]BF₄, however, gave an unexpected bis(diphenylphosphinito)difluoroborate complex, $[Co(Me_2dtc)_2((Ph_2PO)_2BF_2)]$ (1). Here, we describe the molecular and crystal structure and spectroscopic

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characterization of complex **1** in comparison with those of the corresponding Ph_2POMe complex, as well as the formation of bis(diphenylphosphinito)difluoroborate anion.

2. Experimental

2.1. Materials

Chlorodiphenylphosphine (PClPh₂), tetramethylthiuram disulfide (Me₂NC(S)S–SC(S)NMe₂) and other chemicals and solvents were commercially available, and they were used as received. The complexes, *trans*-[Co(Me₂dtc)₂(PPh₃)₂]BF₄ [4] and *cis*-[Co(Me₂dtc)₂(PHPh₂)₂]BF₄ [3], were prepared by the methods reported previously.

2.2. Preparation of $[Co(Me_2dtc)_2\{(Ph_2PO)_2BF_2\}]$ (1)

2.2.1. Method A

Under a dinitrogen atmosphere PClPh₂ (1.21 g, 5.48 mmol) was added dropwise to an ethanol solution (60 cm^3) of $Co(BF_4)_2 \cdot 6H_2O$ (0.793 g, 2.33 mmol), and the mixture was refluxed for 24 h. After cooling the mixture in an ice bath, a solution of tetramethylthiuram disulfide (0.503 g, 2.09 mmol) in a mixture of dichloromethane and ethanol (1:1, 30 cm³) was added dropwise for 2 h. The resulting green precipitate of [$Co(Me_2dtc)_3$] was filtered off, and the filtrate was concentrated under reduced pressure, affording a





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greenish oily residue. The residue was dissolved in a minimum amount of methanol, and the solution was subjected to column chromatography using Sephadex LH-20 resin. A red band was eluted with methanol, and the eluate was evaporated at room temperature and ambient pressure to give a red precipitate. The precipitate was collected by filtration and recrystallized from methanol by vapor diffusion of diethyl ether, depositing red block crystals. Yield: 54.6 mg (3.5%). *Anal.* Calc. for $C_{30}H_{32}BCOF_2N_2O_2P_2$. S₄: C, 48.01; H, 4.30; N, 3.73. Found: C, 47.30; H, 4.05; N, 3.61%. ¹H NMR (CDCl₃, 400 MHz, 22 °C): δ 2.47 (s, N–CH₃, 6H), 2.80 (s, N–CH₃, 6H), 7.12 (t, Ph, *J* = 7.3 Hz, 4H), 7.21 (t, Ph, *J* = 7.3 Hz, 2H), 7.40–7.48 (m, Ph, 6H), 7.67–7.71 (m, Ph, 4H), 8.00–8.07 (m, Ph, 4H). IR (KBr disc): ν (B–F) 1096 cm⁻¹, ν (P–O) 1005 cm⁻¹.

2.2.2. Method B

To an acetonitrile solution (3 cm^3) of cis-[Co(Me₂dtc)₂ (PHPh₂)₂]BF₄ (49.5 mg, 0.065 mmol) was added a methanol solution (1 cm^3) of LiBF₄ (12.2 mg, 0.13 mmol) and an aqueous NaOH solution (5.9 mg, 0.15 mmol, 1 cm³). The mixture was stirred in the dark for 24 h at room temperature, and the resulting green precipitate was filtered off. The brown filtrate was evaporated under reduced pressure, and the resulting oily residue was extracted with dichloromethane. The filtered extract was concentrated to ca. 2 cm³ by flow of dry nitrogen, and the red brown concentrate was subjected to column chromatography using Sephadex LH-20 resin. A major red band and a minor green band were eluted with methanol. The major red eluate was evaporated to dryness under reduced pressure, and the resulting crude product was recrystallized from dichloromethane/methanol by slow evaporation of the solvents at room temperature, depositing red block crystals. Yield: 7.8 mg (16%).

2.3. Measurements

Infrared spectra were measured on a JASCO FTIR-001 spectrophotometer using KBr disc method. UV–Vis absorption spectra were recorded on a JASCO V-550 spectrophotometer at room temperature. Proton and phosphorus-31 NMR spectra were acquired on a Varian 400-MR spectrometer at 22 °C. The ¹H NMR chemical shifts were referenced to the residual ¹H NMR signals of the deuterated solvents and are reported versus TMS. The ³¹P NMR chemical shifts were referenced to the external 85% H₃PO₄.

Table	1
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Chemical formula	C ₃₀ H ₃₂ BCoF ₂ N ₂ O ₂ P ₂ S ₄
Formula weight	750.50
Т (К)	188(2)
Crystal color and shape	red, block
Size of specimen (mm)	$0.20\times0.20\times0.20$
Crystal system	triclinic
Space group	ΡĪ
Z	4
a (Å)	13.7205(7)
b (Å)	14.4337(8)
c (Å)	17.7699(8)
α (°)	105.946(2)
β (°)	90.256(2)
γ (°)	91.363(2)
$U(Å^3)$	3380.8(3)
D_{calc} (Mg m ⁻³)	1.474
μ (Mo K α) (mm ⁻¹)	0.892
R _{int}	0.081
$R_1 (F^2: F_o^2 > 2\sigma(F_o^2))$	0.065
wR_2 (F^2 : all data)	0.190
Goodness-of-fit (GOF) on F^2	1.073

2.4. X-ray crystallographic study

The X-ray diffraction data of **1** were obtained at -85(2) °C on a Rigaku R-axis rapid imaging plate detector with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). A suitable crystal was mounted with a cryoloop and flash-cooled by cold nitrogen stream. Data were processed by the Process-Auto program package [12], and absorption corrections were applied by the numerical integration method from crystal shape [13]. The structure was solved by the direct method using SIR2004 [14], and refined on F^2 (with all independent reflections) using SHEIXL97 program [15]. All non-H atoms were refined anisotropically. Hydrogen atoms were introduced at the positions calculated theoretically and treated with riding models. All calculations were carried out using CRYSTALSTRUC-TURE software package [16].

Crystal data are collected in Table 1.

3. Results and discussion

3.1. Preparation and structural characterization of cobalt(III) complex

According to the synthetic methods for trans- and cis-[Co(Me2 $dtc)_2(PHPh_2)_2[BF_4 [3]]$, we have tried to prepare the analogous PClPh₂ complexes. Firstly, the ligand substitution of PClPh₂ for PPh₃ in trans-[Co(Me₂dtc)₂(PPh₃)₂]BF₄ was attempted, likewise to the preparation of *trans*-[Co(Me₂dtc)₂(PHPh₂)₂]BF₄. However, the reaction gave a complicated mixture of products, and no complex could be isolated from the mixture except for [Co(Me₂dtc)₃] and trans-[Co(Me₂dtc)₂(PPh₃)₂]BF₄. Then, we examined an oxidative addition of tetramethylthiuram disulfide to a mixture of cobalt(II) tetrafluoroborate and PCIPh₂. In the case of PHPh₂ this method gave the cis-isomer of [Co(Me₂dtc)₂(PHPh₂)₂]BF₄. When PClPh₂ was added to a pale pink solution of Co(BF₄)₂·6H₂O in ethanol, the color of reaction mixture immediately turned to blue, unlike for PHPh₂ which afforded a reddish brown solution. To this mixture was added a solution of tetramethylthiuram disulfide in a mixture of dichloromethane and ethanol. This reaction also gave a complicated mixture of products, and the main product was green $[Co(Me_2dtc)_3]$. After removal of $[Co(Me_2dtc)_3]$ by washing with diethyl ether, the residue was subjected to column chromatography (Sephadex LH-20), and a red band was collected by elution with methanol. From the eluate red crystals of 1 were obtained. Although the yield of **1** was only a few percent, it was reproducible in several experiments.

The molecular and crystal structure of **1** was determined by Xray crystallography. It was found that compound **1** crystallized in a triclinic space group $P\bar{1}$ with Z = 4. There are two crystallographically independent complex molecules in the asymmetric unit, and both molecules are similar in structure, as shown in Fig. 1. It was revealed that these complexes contain an anionic $Ph_2POBF_2OPPh_2^-$ ligand, which forms a six-membered chelate ring. The chelate ring in molecule 1 (with Co1) has a skew conformation, while that in molecule 2 (with Co2) has a distorted envelope conformation. Regardless, the chelate bite angles are very similar to each other: 93.44(4)° versus 93.21(4)°. The average P–O, O–B and B–F bond lengths in **1** are 1.574(6), 1.46(1) and 1.38(1) Å, respectively. These bond lengths are comparable to those of the previously reported R₂POBF₂OPR₂⁻ complexes [17–19].

The above-mentioned P–O bonds (average 1.574(6) Å) are shorter than those of *cis*-[Co(Me₂dtc)₂(Ph₂POMe)₂]BF₄ (average 1.604(4) Å), which has the same coordination environment with monodentate phosphinite (Ph₂POMe) [2]. The Co–P bond lengths in **1** are in the range of 2.222(1)–2.234(1) Å (average 2.227(2) Å), which are also a little shorter than those in *cis*-[Co(Me₂dtc)₂(Ph₂POMe)₂]BF₄ (average 2.245 Å). These bond shortenings are



Fig. 1. ORTEPS (50% probability level, H-atoms omitted for clarity) of two crystallographically independent molecules of [Co(Me₂dtc)₂{(Ph₂PO)₂BF₂}] (1).

probably caused by the anionic nature, as well as the chelate effect, of bidentate $Ph_2POBF_2OPPh_2^{-1}$ ligand.

The Co–S bonds in **1** showed a significant difference between the chemically non-equivalent bonds. The Co–S bonds *trans* to P donor (average 2.304(2) Å) was apparently longer than the mutually *trans* Co–S bonds (average 2.260(2) Å), indicating a strong *trans* influence of Ph₂POBF₂OPPh₂[–]. This extent of elongation by the bis(phosphinito)borate (~0.04 Å) is much larger than that by Ph₂-POMe (~0.02 Å) [2].

3.2. ¹H NMR and visible absorption spectra

In the ¹H NMR spectrum of **1** in CDCl₃ two resonances for N–CH₃ were observed at δ 2.47 and 2.80, corresponding to the molecular C_2 symmetry of complex **1**. Also, the spectral patterns for the phenyl protons were consistent with the proposed molecular C_2 symmetry. Thus, it is concluded that the molecular



Fig. 2. Absorption spectra of $[Co(Me_2dtc)_2{(Ph_2PO)_2BF_2}]$ (blue solid line) and *cis*- $[Co(Me_2dtc)_2(Ph_2POMe)_2]BF_4$ (red broken line) in visible region (in acetonitrile at room temperature). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

structure obtained by X-ray analysis (Fig. 1) is maintained in solution.

Fig. 2 compares the visible absorption spectrum of complex **1** with that of *cis*-[Co(Me₂dtc)₂(Ph₂POMe)₂]BF₄. The first and the second d–d transition bands of **1** are observed at 19600 cm⁻¹ (ε = 822 M⁻¹ cm⁻¹) and 24300 cm⁻¹ (ε = 3350 M⁻¹ cm⁻¹), respectively, which are relatively blue-shifted from those of *cis*-[Co(Me₂-dtc)₂(Ph₂POMe)₂]BF₄ (18330 and 23200 cm⁻¹). This indicates that the ligand-field strength of anionic (Ph₂PO)₂BF₂⁻ is moderately stronger than that of a neutral Ph₂POMe, being consistent with the above-mentioned difference in their Co–P bond lengths.

3.3. Formation of $(Ph_2PO)_2BF_2^-$ and its cobalt(III) complex

In this study the formation of bis(diphenylphosphinito)difluoroborate anion. Ph₂POBF₂OPPh₂⁻, from chlorodiphenvlphosphine was observed [20,21]. In the first place of this conversion, PCIPh₂ would presumably be hydrolyzed in wet ethanol to give Ph₂P(O)H. The ³¹P{¹H} NMR spectrum of PCIPh₂ in CDCl₃ gave a single resonance at δ 82.33 (Fig. 3*a*); however, a CD₃OD solution of PClPh₂ gave a completely different spectrum, as shown in Fig. 3b. The main resonance at δ 24.33 was a characteristic triplet with J_{P-D} = 76 Hz. A commercially available diphenylphosphine oxide, Ph₂P(O)H, gave a singlet ${}^{31}P{}^{1}H{}$ NMR signal at δ 22.11 in CDCl₃ (Fig. 3c), but in CD₃OD the phosphine oxide showed a triplet (δ 24.17, J_{P-D} = 75 Hz; Fig. 3d) due probably to a H/D exchange on P atom. These experiments suggested that PCIPh₂ was easily hydrolyzed to give Ph₂P(O)D in CD₃OD. In wet ethanol a similar hydrolysis would take place to give a diphenylphosphine oxide and a chloride anion, the latter of which seemed to be responsible for a blue color of a mixture of Co(BF₄)₂·6H₂O and PClPh₂ in ethanol. Duncan et al. suggested the same hydrolysis of PCIPh₂ in the preparation of rhodium(III) and iridium(III) complexes bearing a hydrogen-bonded Ph₂PO-H···OPPh₂ ligand [20,21].

The most annoying result in this study is a very low yield of the $(Ph_2PO)_2BF_2$ complex, **1**. We have also attempted to prepare complex **1** using $Ph_2P(O)H$, instead of PClPh₂, but the yield was not improved. In solution diphenylphosphine oxide exists as an equilibrium mixture with its valence tautomer of diphenyl(hydroxyl)phosphine, $Ph_2P(OH)$, which acts as a P-donor ligand to a soft metal ion [18,19], but cobalt(II) ion can not be a suitable Lewis acid for formation of its $Ph_2P(OH)$ complex. Thus, little formation of a precursor for complex **1**, that is *cis*-[Co(Me_2dtc)_2(Ph_2POH)_2]⁺ or [Co(Me_2dtc)_2(Ph_2PO-H···OPPh_2)], in the oxidation products from an ethanolic reaction mixture of mixture of a precursor for complex **1**.



Fig. 3. ³¹P{¹H} NMR spectra (22 °C, 162 MHz) of (a) PCIPh₂ in CDCl₃, (b) PCIPh₂ in CD₃OD, (c) Ph₂P(O)H in CDCl₃, and (d) Ph₂P(O)H in CD₃OD.

Co(BF₄)₂, PCIPh₂ {or Ph₂P(O)H} and tetramethylthiuram disulfide would be responsible for the low yield of complex **1**. Once a bis(Ph₂POH) complex or a hydrogen-bonded Ph₂PO-H···OPPh₂ complex was formed, conversion to the corresponding (Ph₂PO)₂-BF₂⁻ complex by a reaction with BF₃·Et₂O or BF₄⁻ anion was well established previously for the rhodium(III), iridium(III), palla-dium(II) and platinum(II) complexes [20–23].

As another preparative method for complex **1**, we have also attempted to hydrolyze the corresponding diphenylphoshine complex, *cis*-[Co(Me₂dtc)₂(PHPh₂)]BF₄, in a mixture of acetonitrile and methanol. To avoid a *cis* to *trans* isomerization of the PHPh₂ complex **[3]**, the mixture was shielded during the reaction. This method gave complex **1** in a little better yield (~16%), but a large amount of [Co(Me₂dtc)₃] was still formed as a byproduct.

4. Conclusion

During a reaction of an ethanolic mixture of PCIPh₂ and $Co(BF_4)_2$ with tetramethylthiuram disulfide, a small but an explicit amount of anionic bis(diphenylphosphinito)difluoroborate was formed via the hydrolysis of PCIPh₂, and its cobalt(III) complex, $[Co(Me_2dtc)_2\{(Ph_2PO)_2BF_2\}]$ (1), was isolated and confirmed by the X-ray crystallographic analysis. It was also revealed that the anionic bis(phosphinito)borate ligand gave a shorter Co–P coordination bond and a larger ligand-field strength than the corresponding neutral phosphinite, Ph₂POMe.

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Appendix A. Supplementary material

CCDC 942321 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.10.028.

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