Inorganica Chimica Acta, 61 (1982) 261–264

Ligand Substitution at a Hexa-coordinate Centre. Reaction of $[Co_2(Et_2dtc)_5]BF_4$ with some Dithiooxamides.
Part I. Synthesis and Characterization of $[Co(Et_2dtc)_2DTO]BF_4$ Complexes

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Received November 11, 1981

New mixed-ligand cobalt(III) dithiocarbamato complexes of the general formula $[Co(Et_2dtc)_2DTO]BF_4$ *(where* Et_2dtc *= diethyldithiocarbamato, and DTO is a dithio-oxamide, in particular: unsubstituted dithio-oxamide =* H_2DTOH_2*; N,N'-diisopropylDTO =* Pr_2DTOH_2 *= N,N'-dicyclohexylDTO =* Hex_2DTOH_2*; N,N'-difurfurylDTO =* Fur_2DTOH_2*; N,N'-dibenzyl-DTO =* Bz_2DTOH_2*; N,N'-diethylDTO =* Et_2DTOH_2*, N,N,N',N'-tetraethylDTO =* Et_4DTO*) have been prepared, characterized by elemental analysis and conductivity measurements, and investigated by vibrational and electronic spectroscopy.*

On these bases it is proposed that the dithio-oxamides act as bidentate sulphur ligands.

Introduction

We are currently interested in the ligand substitution process occurring at octahedral transition metal(III) dithio- or diseleno-carbamato complexes. Our aim is to study this kind of substitution kinetically in order to point out the mechanism of the reaction, and to characterize new mixed-ligand complexes in order to compare the donor ability of sulphur and of selenium atoms when contained in different ligands.

The synthesis of mixed ligand species is very difficult to reach starting from $Co(R_2dtc)_3$, because of its kinetic inertness [1].

Discussing the properties of the $[Co_2(Et_2dtc)_5]BF_4$ complex, Martin *et al.* [2] pointed out the important finding that this product may be a ready source of a reactive Co(III) unit, and they prepared new mixed ligand species as $[Co(Et_2dtc)_2L]$, where L is a mononegative chelating ligand as acetylacetonate, dithioacetylacetonate, dithiocarbonate and dithiocarbamate. Following this, using dithio-oxamides as neutral ligands, we isolated in almost quantitative yields the products $[Co(Et_2dtc)_2DTO]BF_4$.

The dithiooxamide ligands may act as sulphur or nitrogen donors; so far inferences in favour of sulphur and/or nitrogen donation rely mostly on IR evidence.

The kinetic study of the reaction is reported in a second paper (part II).

Experimental

Reagents

H_2DTOH_2 Fluka reagent grade was used without further purification.

The N-substituted derivatives were prepared according to literature methods [3].

The complex $[Co_2(Et_2dtc)_5]BF_4$ was synthesized as reported in [2].

Complexes

In a typical reaction, equimolecular amounts of the reactants were allowed to react in CH_2Cl_2 for one hour under reflux. The solvent was evaporated to dryness and the crude product, extracted with minimum ethanol, left a green solid (characterized as $Co(Et_2dtc)_3$) in quantitative yield according to the reaction scheme:

$$[Co_2(Et_2dtc)_5]BF_4 + DTO \rightarrow Co(Et_2dtc)_3 + [Co(Et_2dtc)_2DTO]BF_4$$

From the ethanolic solution, the diamagnetic product $[Co(Et_2dtc)_2DTO]BF_4$ precipitated quantitatively by addition of petroleum ether and was recrystallized from CH_2Cl_2/ligroine.

C.H.N. elemental analyses were performed by Istituto di Chimica Organica Università di Milano, and the Co was determined by A.A. using a Perkin Elmer mod. 603 Instrument. The analytical data are reported in Table I. Infrared spectra were recorded either as $CHCl_3$ solution or as KBr pellets with a Perkin Elmer mod. 325 Spectrophotometer

UV–visible spectra were carried out in CH_2Cl_2 solutions with a Perkin Elmer mod. 402 spectro-

0020-1693/82/0000-0000/$02.75

TABLE I. Analytical Data.

	Found (calcd)				
	C%	H%	N%	Co%	Colour
$[Co(Et_2dtc)_2H_2DTOH_2]BF_4$	25.69(25.62)	4.35(4.30)	9.88(9.96)	–	green
$[Co(Et_2dtc)_2Pr_2DTOH_2]BF_4$	34.56(33.43)	5.76(5.61)	9.16(8.67)	8.94(9.11)	green
$[Co(Et_2dtc)_2Hex_2DTOH_2]BF_4$	–	–	–	7.87(8.10)	green
$[Co(Et_2dtc)_2Fur_2DTOH_2]BF_4$	36.50(36.55)	4.52(4.46)	7.78(7.75)	–	green
$[Co(Et_2dtc)_2Bz_2DTOH_2]BF_4$	–	–	–	8.15(8.15)	green
$[Co(Et_2dtc)_2Et_2DTOH_2]BF_4$	31.38(31.07)	5.26(5.21)	9.10(9.06)	–	green brown
$[Co(Et_2dtc)_2Et_4DTO]BF_4$	35.57(35.60)	6.13(5.98)	7.77(8.30)	–	green brown

photometer. Magnetic measurements were performed by the Gouy method with a Newport Equipment magnetometer.

Conductance measurements were obtained using a WTW LBR type conductance bridge. The molar conductivities range around 75 ohm^{-1} cm^2 at 25 °C in about 1×10^{-3} *M* nitromethane solutions as expected for 1:1 electrolytes [4].

Results and Discussion

Analytical data (Table I) and molar conductivities are consistent with a $[Co(Et_2dtc)_2DTO]BF_4$ formulation. The IR broad band centred at 1070 cm^{-1} and the 533–525 cm^{-1} doublet are characteristic of the BF_4 group. The other most important IR bands and their assignments are reported in Table II.

As far as the dtc complexes are concerned, it is well established that the $\nu(CN)$ band falls in the 1450–1550 cm^{-1} region and the $\nu(CS)$ around 1000 cm^{-1} [5], where the dtc group behaves as chelating S–S ligand. We can clearly observe the $\nu(CN)$ band at 1500 cm^{-1} but not the $\nu(CS)$, it being covered by BF_4 absorption. We also observed the $\nu(CoS)$ at 360 cm^{-1}. As far as DTO complexes are concerned the IR assignments follow those of Desseyn and Herman [6, 7]. The thioamides, as with the $R_2NCS_2^-$ group, also do not present a single valence bond structure consistent with all their properties.

In fact two possible structures contribute to the resonance hybrid in the molecule:

I II

$$\overset{-}{R_2N}{-}C{=}S \qquad R_2\overset{+}{N}{=}C{-}S^-$$

giving the CS and CN linkages a partial double-bond character sensitive to electronic and steric effects.

The DTO chelating ligands can coordinate through both the sulphur and/or the nitrogen atoms [8–10]. On coordination of the thiocarbonyl group to the metal, $\nu(CN)$ is expected to increase and $\nu(CS)$ to decrease as a consequence of a greater contribution to the structure II of the resonance hybrid. An opposite shift is expected for N coordination. In the case of S,N coordination [10], $\nu(CN)$ and $\nu(CS)$ are shifted to higher and lower frequencies simultaneously. We observed that $\nu(CN)$ shifts to a higher frequency and $\nu(CS)$ to a lower one.

So we have IR evidence to propose the S,S coordination. *Cis*-planar dithio-oxamides coordinated via sulphur atom exhibit strong intramolecular N–H····N bonds, around 3170 cm^{-1} [11]. The $\nu(NH)$ of our complexes in $CHCl_3$ solutions at 3310 cm^{-1} let suggest that the DTO molecules are (although S,S coordinated) not completely planar (with a dihedral angle between the two thioamide functional group), this releasing the intramolecular NH·····N bond. In the solid state (KBr matrices) the $\nu(NH)$ bands are lowered and split, indicating multiple intermolecular hydrogen bonds.

The electronic spectra of the complexes are reported in Table III. In the hypothesis that in the complexes under investigation the Co(III) diamagnetic centre is still octahedrally coordinated with six sulphur atoms, in agreement with Nikolov [12], who discussed the electronic spectra of $Co(Et_2dtc)_3$ complexes, we attribute the bands at about 38 kK to the intraligand $\pi \rightarrow \pi^*$ transitions, the bands at 32 kK and 26 kK to the metal-to-ligand and the ligand-to-metal charge transfer transitions.

The two principal spin-allowed transitions found at 15.4 kK ($^1A_{1g} \rightarrow {}^1T_{1g}$) and at 20.9 kK ($^1A_{1g} \rightarrow {}^1T_{2g}$) for the $Co(Et_2dtc)_3$ derivative are tentatively assigned for the Et_2DTOH_2 at 16.1, 21.0 kK and for Et_4DTO derivatives at 15.3 kK and at 18.7 kK. (Probably, stronger C.T. bands cover the d–d transition of the other complexes). Using these data we tentatively estimated the ligand field parameters, obtaining respectively $\Delta = 16.1, 17.3$ kK; $B = 212, 306$ K, while the 2.6 value of optical electronegativity of the

TABLE II. Principal Infrared Bands (cm^{-1}).

	ν(NH)		ν(CN)*		ν(CS)**	ν(CoS)**
	**	*	dtox	dtc	dtox	
H_2DTOH_2	3118s, 3210s, 3290s	3465s, 3285ms	1399s	–	836s	–
$[Co(Et_2dtc)_2H_2DTOH_2]BF_4$	3230s, 3290s, 3345m, 3400m	3455sbr	1460vs	1500vs	819m	362vs, 352sh
Pr_2DTOH_2	3030w, 3158vs	3175vs	1505vs	–	893vs	–
$[Co(Et_2dtc)_2Pr_2DTOH_2]BF_4$	3065m, 3180m, 3300m	3320s	1578m	1503vs	852vs	362vs
Hex_2DTOH_2	3020vw, 3158s	3170vs	1512vs	–	873vs	–
$[Co(Et_2dtc)_2Hex_2DTOH_2]BF_4$	3108m, 3250m	3315vs	1573m	1499vs	848m	357vs
Fur_2DTOH_2	3115w, 3125w, 3138w, 3210s	3210vs	1515sh, 1499vs	–	872s	–
$[Co(Et_2dtc)_2Fur_2DTOH_2]BF_4$	3080m, 3210m	3310s (3120mw)	1570m	1499vs	842m	365vs
Bz_2DTOH_2	3080vw, 3190vs	3200vs	1505vs	–	872vs	–
$[Co(Et_2dtc)_2Bz_2DTOH_2]BF_4$	3080m, 3210m	3325vs (3120mw)	1570m	1500vs	850m	365vs
Et_2DTOH_2	3058w, 3165vs, 3385w	3320sh, 3200vs	1515vs	–	833s	–
$[Co(Et_2dtc)_2Et_2DTOH_2]BF_4$	3085m, 3200m	3320vs (3140m)	1575m	1499vs	805w	365vs
Et_4DTO	–	–	1490vs	–	868s	–
$[Co(Et_2dtc)_2Et_4DTO]BF_4$	–	–	1555ms	1500vs	849s	358vs, 348sh

*$CHCl_3$ solutions. **KBr pellets.

TABLE III. Electronic Spectral Data in CH_2Cl_2 (kK (log ε)].

$[Co(Et_2dtc)_2H_2DTOH_2]BF_4$	16.0(3.26)		25.9sh	32.3(4.30)	33.9sh	38.5(4.41)
$[Co(Et_2dtc)_2Pr_2DTOH_2]BF_4$	17.4(3.41)		25.4(4.06)	31.7(4.47)		38.0(4.49)
$[Co(Et_2dtc)_2Hex_2DTOH_2]BF_4$	17.7(3.29)		25.4(3.94)	31.6(4.29)		38.0(4.35)
$[Co(Et_2dtc)_2Fur_2DTOH_2]BF_4$	17.1(3.31)		25.6sh	31.7(4.44)		38.0(4.46)
$[Co(Et_2dtc)_2Bz_2DTOH_2]BF_4$	17.1(3.35)		25.4sh	32.0(4.49)		38.3(4.51)
$[Co(Et_2dtc)_2Et_2DTOH_2]BF_4$	16.1(3.77)	21.0sh	25.4(4.10)	31.1(4.42)		36.0(4.50)
$[Co(Et_2dtc)_2Et_4DTO]BF_4$	15.3(2.80)	18.7sh	25.9sh	31.4(4.45)		37.7(4.60)

sulphur atom is evaluated using the lowest charge transfer value [13]. The good agreement of these parameters with those obtained for $Co(Et_2dtc)_3$, $Co(Et_2xan)_3$ and $Co(Et_2xan)_2(Et_2dtc)$ [14] derivatives suggests that the local symmetry is still roughly octahedral in mixed-ligand Co(III) complexes, and that the DTO ligand does not cause significant changes in crystal field parameters with respect to the dtc ligand.

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