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Cobalt(III) Complexes with Dithiooxamide, N,N'-dimethyl- and N,N'-dicyclohexyl-dithiooxamide: CoL_3X_3 (X = Cl, Br, I, ClO_4)

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Some cobalt(III) complexes, $[CoL_3]X_3$ (X = Cl, Br, I, ClO_4), with dithiooxamide, N,N'-dimethyl- and N,N'-dicyclohexyl-dithiooxamide are described. Their conductivities indicate a weak outer-sphere interaction for bromides and a stronger one for chlorides but none for iodides and perchlorates. The electronic spectra are consistent with an essentially octahedral field. The subshell energy differences (17.5–18.5 kK) indicate an S,N coordination confirmed by the splitting of the ν(CN) and ν(CS) bands of the ligands and by the far infrared bands assignable to ν(CoN) (469–417 cm^{-1}) and ν(CoS) (404–346 cm^{-1}) frequencies. Polarographic results indicate a stepwise reduction.

Introduction

With cobalt(II) and other first transition metal divalent ions tetrasubstituted dithiooxamides form S,S coordinated complexes.[1] Dithiooxamide and N,N'-disubstituted dithiooxamides form, in strong acid media, with some divalent ions such as nickel(II)[2] and copper(II),[3] S,N-coordinated complexes. Since S,N-coordinated complexes of cobalt(III) are not very frequent[4] and on the other hand tris chelate cobalt(III) complexes containing three identical unsymmetrical bidentate ligands have a peculiar interest because of their stereochemistry,[5] we have prepared and studied some cobalt(III) complexes with dithiooxamide (DH_4), N,N'-dimethyl- (Me_2DH_2) and N,N'-dicyclohexyl-dithiooxamide (Ch_2DH_2).

Experimental

The reagents were of the best chemical grade. Acid used: AcOH glacial, HCl (37%), HBr (48%), HI (57%), $HClO_4$ (60%). The complexes were prepared by adding a warm solution of $CoAc_2 \cdot 4H_2O$ (Co) to a warm solution of the ligand (L) as follows. $Co(DH_4)_3Cl_3$: 3.3 m*M* Co in 25 ml AcOH + 4 ml HCl to 10 m*M* L in 50 ml AcOH; immediate precipitation. $Co(DH_4)_3Br_3$: 2.4 m*M* Co in 30 ml AcOH + 10 ml HBr to 6 m*M* L in 70 ml AcOH; precipitation in 2 h. $Co(DH_4)_3I_3$: 3 m*M* Co in 25 ml AcOH + 8 ml HI to 6.3 m*M* L in 60 ml AcOH; precipitation in 2 h. $Co(DH_4)_3(ClO_4)_3$: 3.6 m*M* Co in 20 ml AcOH + 10 ml $HClO_4$ to 11 m*M* L in 50 ml AcOH; immediate precipitation. $Co(Me_2DH_2)_3Cl_3$: 2 m*M* Co in 20 ml AcOH + 10 ml HCl to 8 m*M* L in 50 ml AcOH; by adding EtOH until incipient precipitation and standing at 0° C for 24 h red crystals precipitate. $Co(Me_2DH_2)_3Br_3$: 2 m*M* Co in 20 ml AcOH + 10 ml HBr to 8 m*M* L in 50 ml AcOH; precipitation in 24 h. $Co(Me_2DH_2)_3I_3$: 2 m*M* Co in 20 ml AcOH + 8 ml HI to 8 m*M* L in 50 ml AcOH; precipitation in 24 h. $Co(Me_2DH_2)_3(ClO_4)_3$: 2.4 m*M* Co in 5 ml AcOH + 25 ml $HClO_4$ to 4.8 m*M* L in 25 AcOH; precipitation in 20 h at 0° C. $Co(Ch_2DH_2)_3Cl_3$: 1.7 m*M* Co in 20 ml AcOH + 10 ml HCl to 3.5 m*M* L in 100 ml AcOH; in 4 h a small amount of ligand precipitates; from the filtered solution in 48 h red crystals are obtained. $Co(Ch_2DH_2)_3Br_3$: 1.6 m*M* Co in 200 ml AcOH + 10 ml HBr to 3.4 m*M* L in 100 ml AcOH; by standing 24 h at 0° C red crystals are obtained. $Co(Ch_2DH_2)_3I_3$: 1.6 m*M* Co in 20 ml AcOH + 15 ml HI to 4.8 m*M* L in 130 ml AcOH; precipitation in several hours. $Co(Ch_2DH_2)_3(ClO_4)_3$: 3.5 m*M* Co in 10 ml AcOH + 10 ml $HClO_4$ to 7 m*M* L in 250 ml AcOH + 10 ml $HClO_4$; precipitation in 20 h.

All the complexes are red under the microscope and cannot be recrystallized. They were analysed by conventional methods (Table I).

Magnetic susceptibilities were measured at room temperature by the Gouy method using $Hg[Co(SCN)_4]$ as calibrant.[7] Conductivities were determined at 25° C on 10^{-3} *M* solutions in dimethylformamide with a WTW conductivity bridge. Electronic spectra were recorded with a Beckman DK 1A spectrophotometer using spectral grade solvents; those of the solids were recorded on filter paper wetted with nujol. Infra red spectra were recorded with a Perkin–Elmer 521 spectrophotometer, on KBr pellets (4000–600 cm^{-1}) and nujol mulls on polythene (600–250 cm^{-1}). Polarografic curves were recorded with an AMEL multipurpose polarograph model 563–551/SU at 25 ± 0.5° C and constant drop time (1.5 sec). A SCE calomel electrode was used for

TABLE I. Analytical Results, Found % and (Calcd.%). Molar Conductivities Λ_M ($\Omega^{-1}mol^{-1}cm^2$) in $10^{-3}M$ Solution in Dimethylformamide.

Compound	Co %	C % (*S %)	H %	X %	Λ_M
$Co(DH_4)_3Cl_3$	11.24(11.25)	14.14(13.75)	1.97(1.92)	19.93(20.30)	50
$Co(DH_4)_3Br_3$	8.25(8.94)	10.94(10.92)	2.03(1.83)		163
$Co(DH_4)_3I_3$	6.92(7.36)	9.14(8.99)	1.76(1.51)		208
$Co(DH_4)_3(ClO_4)_3$	8.19(8.23)	26.81(26.88)*		14.92(14.86)	214
$Co(Me_2DH_2)_3Cl_3$	8.81(9.66)	23.01(23.61)	4.06(3.97)	17.06(17.44)	51
$Co(Me_2DH_2)_3Br_3$	7.16(7.93)	19.94(19.37)	3.80(3.25)	31.73(32.25)	153
$Co(Me_2DH_2)_3I_3$	6.36(6.66)	16.16(16.28)	2.35(2.73)		199
$Co(Me_2DH_2)_3(ClO_4)_3$	7.32(7.35)	23.66(23.98)*		12.95(13.26)	214
$Co(Ch_2DH_2)_3Cl_3$	5.78(5.78)	19.14(18.86)*		9.64(10.42)	59
$Co(Ch_2DH_2)_3Br_3$	5.09(5.11)	42.93(43.76)	6.38(6.30)	20.32(20.81)	162
$Co(Ch_2DH_2)_3I_3$	4.75(4.65)	39.00(38.99)	5.81(5.61)		156
$Co(Ch_2DH_2)_3(ClO_4)_3$	4.63(4.87)	15.79(15.89)*		8.76(8.79)	208

reference and the potential values were corrected for the junction potential. The solutions in DMF were 10^{-3} M for the complexes and 0.1 M for $(Et_4N)ClO_4$, used as supporting electrolyte.

Result and Discussion

The use of strong acid media in the complex preparations completely avoids the formation of polymers; in the crystalline complexes thus obtained these dithiooxamides act as bidentate ligands without losing protons as a consequence of the shift of the equilibrium $HL \rightleftarrows H^+ + L^-$ toward the undissociated form. Cobalt(II) ion is quickly oxidized to Co(III) by the reduction of part of the ligand, as is shown by the development of H_2S from the reaction mixtures. The complexes are unstable and in moist air after a few days smell of hydrogen sulphide. All the complexes are soluble in polar solvents, owing to their ionic character.

All these CoL_3X_3 complexes are diamagnetic with $S = 0$ ground state. The molar conductivities (Table I) allow one to exclude any interaction in solution between the anions and the complexes for perchlorates and most of the iodides which behave as 3 : 1 electrolytes. A weak outer-sphere association is shown by the Ch_2DH_2–iodide complex and by the bromides and a much stronger one by the chlorides.

The electronic spectra of the solid complexes and their solutions (Table II; Fig. 1) are very similar with the exception of the solid DH_4 complexes. Bands 1 and 2 are shoulders with an apparently high molar extinction coefficient (800–2000 cm^{-1} $mole^{-1}$ l for band 1 and 5000–9000 for band 2) due to their overlap with the tail of the intense charge transfer band located at about 25 kK. No spin-forbidden bands were observed.

Although the site symmetry around the cobalt atom is certainly not O_h, bands 1 and 2 were used to calculate Δ and B with the method given by Jørgensen.[4] The values of Δ obtained for the complexes in solution locate the ligands in a spectrochemical order: DH_4 (18.5–18.1 kK) > Me_2DH_2 (18.4–17.5 kK) > Ch_2DH_2 (17.9–17.5 kK) which reverses the position of DH_4 with respect to the spectrochemical order found for the corresponding square-planar NiS_2N_2 complexes;[2,8] this effect may be due to the steric hindrance in the N,N′-disubstituted dithiooxamides.

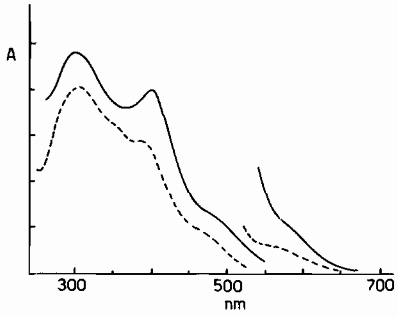

Figure 1. $CHCl_3$ solution spectra of $Co(Ch_2DH_2)_3Cl_3$ (full line) and $Co(Me_2DH_2)_3Cl_3$ (dotted line).

These Δ values are very close to those observed at 18 kK for other $Co^{III}N_3S_3$ complexes[4] and therefore agree with an S,N-coordination of the dithiooxamides to the metal. The very low values (230–285 cm^{-1}) of the interelectronic repulsion parameter B may probably be due rather to a distortion of the octahedral symmetry than to an exceptional nephelauxetic effect of the ligands, as the apparently high intensities of bands 1 and 2 would suggest.

The infrared spectra of the complexes (Table III) show very similar effects of the complexation on some bands of the ligands.[9,10,11] The splittings of the ν(CN) and ν(CS) bands (and of the ν(NH) bands not reported in the table), indicate an S,N-coordination of the

TABLE II. Electronic Spectra (kK, logε in parenthesis) of Octahedral CoL_3X_3 Complexes.

Compound		Band 1	Band 2	Band 3	Band 4	Band 5
$Co(DH_4)_3Cl_3$	solid		19.2 24.7			32.2(4.55)
	EtOH	17.9sh(3.30)	21.3sh	26.0sh		
$Co(DH_4)_3Br_3$	solid		19.1 24.4			
	DMF	17.5sh(3.22)	21.3sh	26.0sh		33.3(4.55)
$Co(DH_4)_3I_3$	solid		17.7sh 23.5			
	DMF	17.4sh(3.28)	21.5sh	25.8sh		33.8(4.56)
$Co(DH_4)_3(ClO_4)_3$	solid		20.0sh 25.1			
	EtOH	17.9sh(3.34)	21.5sh	25.6sh		33.9(4.54)
$Co(Me_2DH_2)_3Cl_3$	solid	17.2sh	20.8sh	25.0		
	$CHCl_3$	17.7sh(2.91)	21.3sh	26.1(4.30)	28.6sh	32.8(4.45)
$Co(Me_2DH_2)_3Br_3$	solid	17.1sh	21.0sh	24.2		
	$CHCl_3$	17.4sh(2.90)	21.1sh	25.6(4.34)	28.8sh	32.6(4.49)
$Co(Me_2DH_2)_3I_3$	solid	17.2sh	20.4sh	25.0		
	DMF	17.5sh(2.91)	21.7sh	27.8(4.45)		33.9(4.55)
$Co(Me_2DH_2)_3(ClO_4)_3$	solid	17.0sh	20.6sh	24.5		
	DMF	17.1sh(2.95)	21.3sh	23.8sh		33.3(4.50)
$Co(Ch_2DH_2)_3Cl_3$	solid	16.9sh	20.3sh	24.7		
	$CHCl_3$	17.0sh(3.01)	20.4sh	25.0(4.45)		33.3(4.53)
$Co(Ch_2DH_2)_3Br_3$	solid	16.8sh	20.2sh	24.4		
	$CHCl_3$	17.1sh(3.06)	20.8sh	25.0(4.47)	27.8sh	34.0(4.55)
$Co(Ch_2DH_2)_3I_3$	solid	17.1sh	20.5sh	26.1		
	$CHCl_3$		20.5sh	25.0sh	27.6(4.43)	33.1(4.57)
$Co(Ch_2DH_2)_3(ClO_4)_3$	solid	17.0sh	20.5sh	25.2		
	$CHCl_3$	17.2sh(3.07)	20.5sh	25.0(4.40)	31.3sh	33.7(4.53)

TABLE III. More Characteristic Infrared Bands (cm^{-1}).

	ν(CN)	ν(RN)	ν(CS)	ν(CoN)	ν(CoS)	Other Far I.R. Bands
DH_4	1423vs		832vs			472m, 407m, 393vw, 293m
CoL_3Cl_3	1470vs, 1308s		1027s, 769vs	430s	346m	392w, 298m
CoL_3Br_3	1460vs, 1290s		1010s, 732vs	427s	380w	396vw, 297m
CoL_3I_3	1457vs, 1270s		992s, 684vs	419ms	370w	293sh
$CoL_3(ClO_4)_3$[a]	1470vs, 1293s		1012s, 735vs	425wb	402m	471w, 291w
Me_2DH_2	1528vs	1154w	867vs			462vw, 284sb
CoL_3Cl_3	1605vs, 1482vs	1216vs, 1102vs	876m, 725sh	466vw, 450vw	397wb, 370sh	266m
CoL_3Br_3	1598vs, 1474vs	1217vs, 1100vs	873m, 725sh	469w, 444m	394wb, 365vw	278ms
CoL_3I_3	1578vs, 1466s	1217s, 1099vs	872m, 690m	468w	386m	275m
$CoL_3(ClO_4)_3$[b]	1590vs, 1478ms	1200s, 1100vsb*	875m, 695mb	463m*	390w	483vw, 279m
Ch_2DH_2	1493vs, (1444ms)	1188vw	868vs			503vs, 443m, 409vs, 339w, 310m
CoL_3Cl_3	1596vs, 1538w, 1452vs	1195sh, 1178s, 1122vs	892s, (698w, 655vs)	436w	378w, 344w	514w, 260s
CoL_3Br_3	1583vs, 1452vs	1196m, 1175s, 1125vs	889s, 659vs	475mb, 467sh	380w, 344w	513m, 258s
CoL_3I_3	1562vs, 1450sh, 1432vs	1197ms, 1172ms, 1123vs	887ms, (715sh, 658vs)	460m, 433w	377wb, 345vw	506m
$CoL_3(ClO_4)_3$[c]	1579vs, 1542sh, 1449vs	1200m, 1172m, 1126vsb*	888s, (755wb, 663vs)	462ms*, 436w	349w	509m, 310wb, 260s

ν(ClO_4): [a] 1100vsb, 923w, 622vs, 471w*; [b] 1100vsb*, 920w, 628vs, 463m*; [c] 1126vsb*, 1025vs, 910m, 622vs, 462ms*.

TABLE IV. Polarographic Data of the $CoL_3(ClO_4)_3$ Complexes.[a]

Complexes	$E_{1/2}^1$, V	$E_{1/2}^2$, V	$E_{1/2}^3$, V	i_{tot}, μA	i_1	i_2	i_3
$Co(DH_4)_3^{3+}$	−0.23	−0.61	−0.92	6.50	1.72	2.13	2.65
$Co(Me_2DH_2)_3^{3+}$	−0.08	−0.53	−0.96	6.85	1.40	2.65	2.80
$Co(Ch_2DH_2)_3^{3+}$	−0.27	−0.80	−0.99	6.65	1.90	2.30	2.45

[a] $E_{1/2}$ *vs* SCE; droptime t = 1.5 sec; T = 25° C; $v_{scan} = 1.7 \times 10^{-3}$ v sec^{-1}; complex = 10^{-3} in DMF using 0.1*M* tetra-ethylammonium perchlorate as supporting electrolyte.

ligands to the metal as in other complexes[2,3,8] of the dithiooxamides.

The strong new bands in the 1220–1100 cm^{-1} region were assigned to ν(R–N) modes and their high intensity was considered as indicative of a coordination through nitrogen stronger than through sulphur.[11]

The assignments of the new far infrared bands to ν(CoN) (475–420 cm^{-1}) and ν(CoS) (400–345 cm^{-1}) are in agreement with this fact and with other literature values: ν(CoN) 415 cm^{-1} for $(Co(NO_2)_6Cs_3$[12] and 450–500 for $Co(NH_3)_6Cl_3$[12] and ν(CoS) 340–360 cm^{-1} for $Co(R\text{-xanthates})_3$ (R = Me, Et).[12]

No polarographic reduction of the free ligands was observed in the same solvent used for the complexes in the range from 0 to −1.1 V. The reduction of the complexes occurs step-wise with three monoelectronic waves (Table IV), the total number of electrons added (n = 3) resulting from the Ilkovič equation.[13] From the shape of the polarographic curves these reductions seem to be irreversible.

A plot of the limiting currents against the droptimes and concentrations shows that the first and second waves are diffusion controlled, while the third wave seems to be adsorption kinetic controlled.

The reductibility of the complexed metal ion depends on the energy difference between the e_g and t_{2g} levels which in turn depends on the ligand field strength.[13] It is therefore likely that the first step of the reduction observed for these complexes occurs at values of $E_{1/2}$ more positive than that given[14] for the first step reduction (−0.51 V) of the complex $Co(NH_3)_6^{3+}$ in 1 *M* $NaHSO_4$ solution.

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