Notes

Synthesis and Characterization of several Mononuclear Cobalt(IV) Dithiocarbamates, $[Co(S_2CNRR')_3]ClO_4$ [R = R′ = Me, Et, or CH_2Ph; R = Me, R′ = Ph; R,R′ = $-(CH_2)_4-$]

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Several mononuclear tris(dithiocarbamato)cobalt(IV) perchlorates, $[Co(S_2CNRR')_3]ClO_4$ [R = R′ = Me, Et, or CH_2Ph; R = Me, R′ = Ph; and R,R′ = $-(CH_2)_4-$] have been prepared by the chemical oxidation of molecular $[Co(S_2CNRR')_3]$ with $Fe(ClO_4)_3$ and characterized. Their visible and i.r. spectroscopic properties are very similar to those of $[Co(S_2CNRR')_3]$ and the dinuclear Co^{III} compounds, $[Co_2(S_2CNRR')_5]BF_4$. They are d^5 low-spin complexes and electrochemical measurements indicate that they are stable 1 : 1 electrolytes in acetone solution.

The ability of *N,N*-disubstituted dithiocarbamate ligands to stabilize unusually high oxidation states of transition-metal ions such as Cu^{III}, Ni^{IV}, Fe^{IV}, and Mn^{IV} is well established.[1–3] However, the reported chemistry of the cobalt dithiocarbamates is conflicting, particularly on the existence of Co^{IV} complexes. Following the successful synthesis of Fe^{IV} and Mn^{IV} dithiocarbamates, Saleh and Straub[4] have prepared two paramagnetic Co^{IV} compounds $[Co(S_2CNEt_2)_3]BF_4$ and $[Co\{S_2CN(C_6H_{11})_2\}_3]BF_4$ by the oxidation of $[Co(S_2CNEt_2)_3]BF_4$ or $[Co\{S_2CN(C_6H_{11})_2\}_3]$ with boron trifluoride. Using the same method, Gahan and O'Connor[5] as well as Hendrickson and Martin[6,7] obtained a series of diamagnetic compounds; an *X*-ray structural analysis[7] has shown that these compounds are the dinuclear Co^{III} species, $[Co_2(S_2CNRR')_5]BF_4$, and not Co^{IV} complexes as claimed by Gahan and O'Connor.[5] Electrochemical data obtained by Bond *et al.*[8] imply that the cobalt(IV) species must exist in solution but appear to have a transient existence. The unsuccessful trials to prepare tris(*N,N*-dicyclohexyldithiocarbamato)cobalt(IV) tetrafluoroborate in the solid state have led these authors to doubt the existence of the paramagnetic cobalt(IV) monomer. We report here the synthesis and characterization of cobalt(IV) compounds obtained by the chemical oxidation of $[Co(S_2CNRR')_3]$ [R = R′ = Me, Et, or CH_2Ph; R = Me, R′ = Ph; R,R′ = $-(CH_2)_4-$] with iron(III) perchlorate.

Experimental

All starting materials and solvents were reagent grade. Electronic spectra were recorded using a Beckman 5240 spectrophotometer and i.r. spectra with a Pye Unicam SP 2000 spectrophotometer. Conductance measurements were made with a CD 810 Tacussel apparatus calibrated with 10^{-3} mol dm^{-3} KCl. Cyclic voltammograms were carried out with an EG and G Princeton Applied Research model 362 instrument; platinum working and auxiliary electrodes were used for all measurements, while the reference electrode was Ag–AgCl (0.1 mol dm^{-3} LiCl, acetone) with 0.1 mol dm^{-3} NEt_4ClO_4 in acetone as solvent (scan rate 200 mV s^{-1}).

The complexes $[Co(S_2CNRR')_3]$ and $[Co_2(S_2CNRR')_5]BF_4$ were prepared as previously described.[9]

Solution Study.—Addition of $Fe[ClO_4]_3 \cdot 9H_2O$ in a mixture of methylene chloride and acetone (80:20) to green solutions of $[Co(S_2CNRR')_3]$ yielded brown solutions. The continuous variations method showed a break at 0.5 indicating a reaction in a 1:1 ratio.

Preparation of Complexes $[Co(S_2CNRR')_3]ClO_4$.—$Fe(ClO_4)_3 \cdot 9H_2O$ (0.52 g, 10^{-3} mol) in acetone (50 cm^3) was slowly added to $[Co(S_2CNRR')_3]$ (10^{-3} mol) in CH_2Cl_2 (100 cm^3). After concentration to 30 cm^3 addition of diethyl ether induced the precipitation of $[Co(S_2CNRR')_3]ClO_4$ as brown solids, except for R = R′ = Et where the resulting dark brown oil was treated again with diethyl ether in order to give the solid. The resulting precipitates were washed and dried under vacuum. **CAUTION:** These compounds must be handled carefully because they have a high tendency to explode.

Results and Discussion

Analytical and physical data for the cobalt(IV) compounds are given in Table 1 together with the data for the mono- and di-nuclear Co^{III} compounds for comparison.

The values Λ_M lie within the expected range (100—160 S cm^2 mol^{-1}) for 1:1 electrolytes at 10^{-3} mol dm^{-3} in acetone[10] (data obtained for NBu_4BF_4 and NBu_4ClO_4 are 145 and 142 S cm^2 mol^{-1} respectively). We note that the molar conductances of the $[Co(S_2CNRR')_3]ClO_4$ and $[Co_2(S_2CNRR')_5]BF_4$ compounds are always similar when the ligands are the same.

Cyclic voltammograms of the $[Co(S_2CNRR')_3]$ and $[Co(S_2CNRR')_3]ClO_4$ compounds are similar, involving the same $[Co(S_2CNRR')_3]^+/[Co(S_2CNRR')_3]$ redox system and thus confirming the existence of cobalt(IV) dithiocarbamates. An example is given in the Figure for the *N,N*-dimethyldithiocarbamato-compounds after repeated sweeping. The electrochemical data obtained without i.r. compensation are listed in Table 2.

The results are in close agreement with those of Bond *et al.*[8] Several reduction and oxidation peaks are observed for the dinuclear compounds, the electrochemical process is complex and appears to be dependent on the ligand. In all cases for different substituents R and R′, the $[Co_2(S_2CNRR')_5]BF_4$ voltammograms are quite different from those of the mononuclear compounds.

The magnetic susceptibilities listed in Table 1 indicate clearly that the cobalt(IV) dithiocarbamates are d^5 low-spin compounds with a large orbital contribution. These Co^{IV} compounds do not exhibit a low spin–high spin equilibrium state at room temperature as observed for the isoelectronic $[Fe(S_2CNRR')_3]$ complexes.

Table 1. Analytical[a] and physical data

Complexes[b]	Analysis C	Analysis H	Analysis N	M	Λ_M[c]/S cm^2 mol^{-1}	χ_M(10^6 c.g.s.u.)[d]	$\mu_{eff.}$/ B.M.[e]
$[Co_2(S_2CNMe_2)_5]BF_4$	21.4 (22.4)	3.8 (3.8)	8.9 (8.7)	805.8	134	Diamagnetic	
$[Co(S_2CNMe_2)_3]ClO_4{\cdot}0.5Me_2CO$	23.0 (23.0)	3.8 (3.9)	7.8 (7.7)	548.1	118	2 300	2.32
$[Co_2(S_2CNEt_2)_5]BF_4{\cdot}H_2O$	31.4 (31.2)	5.3 (5.4)	7.1 (7.3)	964.0	147	Diamagnetic	
$[Co(S_2CNEt_2)_3]ClO_4{\cdot}H_2O$	29.4 (29.0)	5.2 (5.2)	6.5 (6.8)	621.2	153	2 400	2.37
$[Co_2\{S_2CN(CH_2Ph)_2\}_5]BF_4{\cdot}3CH_2Cl_2$	51.2 (51.4)	4.0 (4.2)	4.0 (3.8)	1 821.6	107	Diamagnetic	
$[Co\{S_2CN(CH_2Ph)_2\}_3]ClO_4{\cdot}H_2O$	54.8 (54.4)	4.5 (4.5)	4.2 (4.2)	993.6	98	2 100	2.22
$[Co_2(S_2CNMePh)_5]BF_4{\cdot}H_2O$	43.0 (42.4)	3.9 (3.7)	6.2 (6.2)	1 134.1	133	Diamagnetic	
$[Co(S_2CNMe_2Ph)_3]ClO_4{\cdot}4H_2O$	36.5 (37.1)	3.7 (4.1)	5.0 (5.4)	777.3	135	3 100	2.70
$[Co_2\{S_2CN(CH_2)_3CH_2\}_5]BF_4{\cdot}Me_2CO$	35.3 (35.4)	5.0 (5.0)	7.3 (6.7)	1 052.1	124	Diamagnetic	
$[Co\{S_2CN(CH_2)_3CH_2\}_3]ClO_4{\cdot}0.5Me_2CO$	31.8 (31.6)	4.3 (4.3)	6.7 (6.7)	626.2	117	2 700	2.51

[a] Calculated values are given in parentheses. Analyses were performed in this University or by the Microanalytical service of C.N.R.S. [b] The nature of the crystallization solvent molecules was determined using i.r. spectroscopy and also thermogravimetric analysis for the dinuclear compounds. [c] 10^{-3} mol dm^{-3} in acetone at 20 °C. [d] Magnetic susceptibilities are given after diamagnetic corrections calculated from Pascal's constants (A. Earnshaw, 'Introduction to Magnetochemistry,' Academic Press, London, 1968, p. 4). [e] B.M. = 0.927×10^{-23} A m^2.

Table 2. Cyclic voltammetry data

Complexes	E_{ep}/V	E_{pa}/V	ΔE_p/mV	$E_{\frac{1}{2}}$/V
$[Co(S_2CNMe_2)_3]$	0.975	1.060	85	1.02
$[Co(S_2CNMe_2)_3]ClO_4$	0.99	1.060	70	1.025
$[Co_2(S_2CNMe_2)_5]BF_4$	0.98, 0.58	1.095, 0.66		
$[Co(S_2CNEt_2)_3]$	0.965	1.05	85	1.01
$[Co(S_2CNEt_2)_3]ClO_4$	0.965	1.055	90	1.01
$[Co_2(S_2CNEt_2)_5]BF_4$	0.96, 0.58	*ca.* 1.08, 0.85 (sh)		
$[Co\{S_2CN(CH_2Ph)_2\}_3]$	1.12	1.19	70	1.155
$[Co\{S_2CN(CH_2Ph)_2\}_3]ClO_4$	1.11	1.18	70	1.145
$[Co_2\{S_2CN(CH_2Ph)_2\}_5]BF_4$	1.1 (w), 0.62	1.25 (sh), 0.71		
$[Co(S_2CNMePh)_3]$	1.015	1.105	90	1.06
$[Co(S_2CNMePh)_3]ClO_4$	1.03	1.12	90	1.075
$[Co_2(S_2CNMePh)_5]BF_4$	1.02, 0.625	1.135, 0.88		
$[Co\{S_2CN(CH_2)_3CH_2\}_3]$	0.965	1.045	80	1.005
$[Co\{S_2CN(CH_2)_3CH_2\}_3]ClO_4$	0.98	1.05	70	1.015
$[Co_2\{S_2CN(CH_2)_3CH_2\}_5]BF_4$	*	1.04		

* Several weak peaks.

The infrared spectra of the dinuclear cobalt(III) and the cobalt(IV) compounds are similar to those of the $[Co(S_2CNRR')_3]$ complexes. Additional broad bands centred at 1 070 and 1 100 cm^{-1} respectively confirm the presence of the BF_4^- and ClO_4^- anions. Comparison of the spectra of $[Co(S_2CNRR')_3]$ and $[Co(S_2CNRR')_3]ClO_4$ reveals only an increase (*ca.* 20 cm^{-1}) in the $C\overset{\cdots}{-}N$ band (*ca.* 1 500 cm^{-1}) as is usually observed with oxidation of the metal: the bands are observed at 1 550, 1 520, 1 510, 1 495, and 1 520 cm^{-1} for the Me, Et, CH_2Ph, MePh, and $-(CH_2)_4-$ dithiocarbamates of cobalt(IV) and at 1 530, 1 495, 1 485, 1 490, and 1 490 cm^{-1} for the corresponding cobalt(III) complexes. We also note that practically the same shifts of $\nu(C\overset{\cdots}{-}N)$ to higher energies (respectively 1 550, 1 510, 1 520, 1 490, and 1 510 cm^{-1}) are observed in the dinuclear compounds in agreement with data of Hendrickson *et al.*[7]

The electronic spectra of all the compounds are quite similar apart from slight changes in positions and intensities of the absorption bands, in particular the weak band around 650 nm appears as a symmetrical band for $[Co(S_2CNRR')_3]$ and $[Co_2(S_2CNRR')_5]BF_4$ but as a shoulder for $[Co(S_2CNRR')_3]ClO_4$. The spectra of the Co^{IV} dithiocarbamates are in close agreement with the spectra given by Saleh and Straub[4] for $[Co\{S_2CN(C_6H_{11})_2\}_3]BF_4$.

Conclusions

Our study has clearly shown that besides $[Co(S_2CNRR')_3]$, known long ago,[11] and the well described[6,7] dinuclear compounds $[Co_2(S_2CNRR')_5]BF_4$ there also exist paramagnetic Co^{IV} dithiocarbamates of the type $[Co(S_2CNRR')_3]ClO_4$. Spectroscopic data are analogous for these compounds and therefore are not conclusive to their identifications and can explain the conflicting data on the existence of Co^{IV}

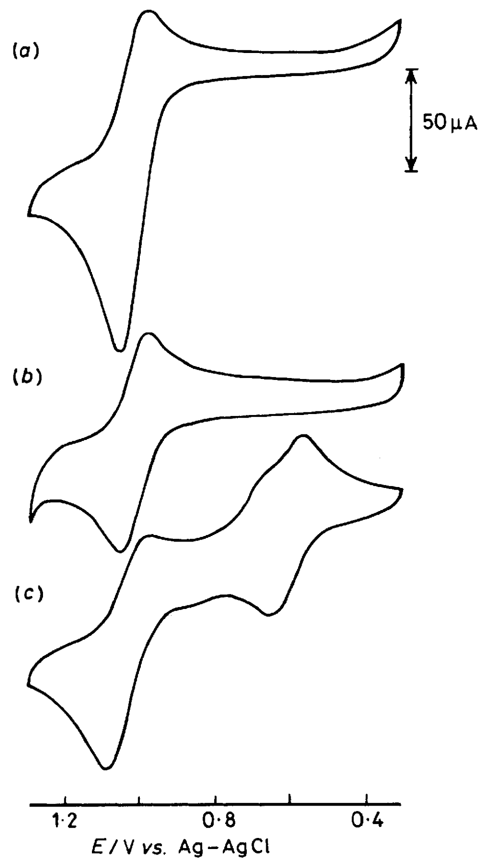

Figure. Cyclic voltammograms at a platinum electrode of (*a*) $[Co(S_2CNMe_2)_3]$, (*b*) $[Co(S_2CNMe_2)_3]ClO_4$, and (*c*) $[Co_2(S_2CNMe_2)_5]BF_4$ in acetone (0.1 mol dm^{-3} NEt_4ClO_4); scan rate = 200 mV s^{-1}

dithiocarbamates. Moreover $[Co\{S_2CN(C_6H_{11})_2\}_3]BF_4$ and $[Co_2(S_2CNRR')_5]BF_4$ are prepared in a similar manner by the action of BF_3 or $Et_2O{\cdot}BF_3$ in the presence of oxygen on molecular $[Co(S_2CNRR')_3]$; the dinuclear species were presumably obtained *via* an oxidation pathway.[7] This hypothesis is confirmed by the fact that recrystallization of the Co^{IV} compounds sometimes led to the dinuclear compounds. Only magnetic and electrochemical measurements (molar conductance and cyclic voltammetry) have permitted the characterization of the Co^{IV} and the dinuclear Co^{III} dithiocarbamates. As the $[Co\{S_2CN(CH_2Ph)_2\}_3]^+/[Co\{S_2CN(CH_2Ph)_2\}_3]$ redox system has the highest $E_{\frac{1}{2}}$ value of all the Co^{III} dithiocarbamates generally used,[8] oxidation by iron(III) ions seems a good way to obtain all the Co^{IV} compounds, following the reaction

$$[Co(S_2CNRR')_3] + Fe^{3+} \xrightarrow{X^-} [Co(S_2CNRR')_3]^+ + Fe^{2+}$$

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