COBALT(III) COMPLEXES WITH MIXED CHELATING LIGANDS

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As recently was reported (1) potassium bis biuretato-cobaltate(III) $[\text{KCo}(\text{bi})_2]$, which shows a striking magnetic behavior having a spin-triplet ground state, forms diamagnetic bis adducts with monodentate nitrogenous bases. The existence of successful addition reactions of this type and our interest (2) in complexes with dithioligands prompted the investigation of the reaction of $\text{KCo}(\text{bi})_2$ with N,N-dialkyldithiocarbamate ion (R_2dte^-) and O-alkylxanthate ion (Rxn^-) respectively.

It is found that, when equivalent amounts of $\text{KCo}(\text{bi})_2$ and R_2dte^- are reacted in aqueous solution, the initial suspension of $\text{KCo}(\text{bi})_2$ disappears, and a blue-violet complex ion $[\text{Co}(\text{bi})_2(\text{R}_2\text{dte})]^{2-}$ is formed according to the reaction equation:

This reaction had to be carried out at 0° , because otherwise the green complex ion $\text{Co}(\text{bi})(\text{R dte})^-$ is rapidly formed. The formation of the latter ion is favored, when two instead of one equivalent R_2dte^- are used and when the reaction is carried out at room temperature. The reaction equation is:

It seemed not preferable to use an excess of R_2dtc^- in the latter reaction because in that case the competitive formation of $\text{Co}(\text{R}_2\text{dtc})_3$ (insoluble in aqueous solution) becomes important. Often, the isolation of the complex ions appeared to be difficult; we only succeeded in preparing $\text{K}_2\text{Co}(\text{bi})_2(\text{Et}_2\text{dtc}) \cdot 3 \text{H}_2\text{O}$ and $\text{NBu}_4\text{Co}(\text{bi})(\text{Bu}_2\text{dtc})_2$ in pure state. These complexes are diamagnetic in the solid state at room temperature, as can be expected for an approximately octahedral Co^{+3} ion with a d^6 configuration. Conductivity studies, performed in nitrobenzene solution at 25° on $\text{NBu}_4\text{Co}(\text{bi})(\text{Bu}_2\text{dtc})_2$, proved this compound to be a 1:1 electrolyte.

Using R_{xan}^- instead of R_2dtc^- in the above reactions, products are formed, whose colors (blue-violet and green respectively), suggest the existence of the complex ions $[\text{Co}(\text{bi})_2(\text{R}_{\text{xan}})]^{2-}$ and $[\text{Co}(\text{bi})(\text{R}_{\text{xan}})_2]^-$ respectively. These complex ions have so far not been isolated.

The combined results are clear evidence for the formation of the six-coordinated Co(III) ions $\text{Co}(\text{bi})_2\text{L}^{2-}$ and $\text{Co}(\text{bi})\text{L}_2^-$, when $\text{KCo}(\text{bi})_2$ is reacted with a monoanionic chelating dithioligand L.

It was also possible to prepare $\text{Co}(\text{Et}_{\text{xan}})(\text{Et}_2\text{dtc})_2$ by reacting appropriate amounts of $\text{Co}(\text{Et}_{\text{xan}})_3$ and $\text{Co}(\text{Et}_2\text{dtc})_3$ in chloroform. The PMR spectrum of $\text{Co}(\text{Et}_{\text{xan}})(\text{Et}_2\text{dtc})_2$ proves the octahedral coordination symmetry of the cobalt showing a complicated fine structure for the $\text{N}-\text{CH}_2$ proton resonances (fig.). The latter is due to the diastereotropic

nature of the N—CH₂ protons. Such a phenomenon was recently reported (3) for the methylene proton resonance bands of $\left[\text{Fe}(\text{Et}_2\text{dtc})_2(\text{S}_2\text{C}_2(\text{CF}_3)_2)\right]^{2-}$.

Figure. The PMR spectrum of $\text{Co}(\text{Etxan})(\text{Et}_2\text{dtc})_2$ recorded in CDCl_3 solution at 30° .

The AB pattern of the N—CH₂ proton resonances, shown in the figure, may be satisfactorily explained by assuming that the coupling between the diastereotropic protons (14 Hz) is twice as strong as that with the methyl protons (7 Hz). It is rather peculiar, however, that the diastereotropic nature of the O—CH₂ protons did not show in PMR. In this connection it has to be mentioned that for the complexes $\text{Co}(\text{Et}_2\text{dtc})_3$, $\text{Co}(\text{Etxan})_3$ and $\text{Ni}(\text{Et}_2\text{dtc})_3^+$ (2) in CDCl_3 at room temperature only one quartet for the methylene proton resonances is observed, which is due to coupling with the methyl protons. The recording of temperature-dependent PMR spectra will be subject of further investigations. Upon cooling the difference in chemical shift of the diastereotropic dithiocarbamate protons in $\text{Co}(\text{Etxan})(\text{Et}_2\text{dtc})_2$ increases slightly. Furthermore one might expect an extra

splitting of the N-bonded ethyl resonances (of the methylene as well as of the methyl proton resonances) due to restricted rotation around the C $\equiv$ N bond (3, 4, 5). At temperatures as low as +9 $^{\circ}$ such a splitting was not observed, probably because at that temperature the hindering of internal rotation is too small. We have indications that the AB pattern is also found for the N—CH $_2$ dithiocarbamate proton resonances of NBu $_4$ Co(bi)(Bu $_2$ dtc) $_2$. However, due to the overlap with the absorption bands of the cation (N—CH $_2$) a well-defined interpretation was not possible so far. Moreover, the interpretation will be difficult in view of the coupling of the N—CH $_2$ dithiocarbamate protons with α , β and γ protons by which the fine structure is broadened considerably with respect to that of the diethyldithiocarbamates.

Infrared spectra

In the IR spectra of the various new Co complexes $\nu(\text{C}\equiv\text{N})$ is a good measure for the electron donating capacity of the ligands with respect to the dithiocarbamate ligand (table I). It is found that in the mixed biuretato-dithiocarbamate complexes no shift of any importance as compared to that determined for Co(Et $_2$ dtc) $_3$ can be observed. Therefore, it may be concluded that the electron donating capacity of the biuretato ligand will be roughly equal to that of the Et $_2$ dtc $^-$ ligand. For Co(Etxan)(Et $_2$ dtc) $_2$ the C $\equiv$ N stretching frequency is found at a higher wavenumber than for Co(Et $_2$ dtc) $_3$. The C—O stretching frequency, which is characteristic of the xantnate ligand is found to be lower for Co(Etxan)(Et $_2$ dtc) $_2$ than for Co(Etxan) $_3$. Both

findings can be ascribed to the fact that the electron releasing effect of the —NR_2 group is stronger than that of the —OR group.

TABLE I

IR data of some Co(III) complexes.

	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{C}=\text{O})$ in cm^{-1}
$\text{K}_2\text{Co}(\text{bi})_2(\text{Et}_2\text{dtc}) \cdot 3 \text{H}_2\text{O}$	1495	
$\text{KCo}(\text{bi})(\text{Et}_2\text{dtc})_2$	1495	
$\text{Co}(\text{Et}_2\text{dtc})_3$	1490	
$\text{Co}(\text{Etxan})(\text{Et}_2\text{dtc})_2$	1505	1230
$\text{Co}(\text{Etxan})_3$		1250

TABLE II

d-d transitions in Co(III) complexes. The band frequencies and Δ are given in kK, B in K. The molar extinction coefficient is given in parentheses. Unless otherwise reported, the spectra were recorded in CHCl_3 solution.

$\text{K}_2\text{Co}(\text{bi})_2(\text{Et}_2\text{dtc}) \cdot 3 \text{H}_2\text{O}^*$	15.9			
$\text{NBu}_4\text{Co}(\text{bi})(\text{Bu}_2\text{dtc})_2$	15.0 (500)		20.8 ?	
$\text{Co}(\text{bi})_2(\text{Etxan})^-$ ***	17.5			
	ν_1	ν_2	Δ	B
$\text{Co}(\text{Et}_2\text{dtc})_3$ (7)	15.5 (600)	20.8 sh	16.3	375
$\text{Co}(\text{Etxan})(\text{Et}_2\text{dtc})_2$	15.7 (470)	21.1 sh	16.5	380
$\text{Co}(\text{Etxan})_3$.	16.0 (330)	20.7 sh	16.8	328

sh = shoulder; * reflectance spectrum (in BaSO_4); ** re-corded in aqueous solution.

UV-VIS spectra

For the series of complexes $\text{Co}(\text{Et}_2\text{dtc})_3$, $\text{Co}(\text{Et}\text{xan})_3$ and $\text{Co}(\text{Et}\text{xan})(\text{Et}_2\text{dtc})_2$ the crystal field splitting energy Δ and the Racah parameter B were calculated from UV-VIS spectral data (according to Jørgensen (6)) assuming a low spin d^6 Co^{+3} ion with a local O_h symmetry. The tabulated values of Δ and B of $\text{Co}(\text{et}\text{xan})(\text{Et}_2\text{dtc})_2$ show a good correspondence with those of $\text{Co}(\text{Et}_2\text{dtc})_3$ and $\text{Co}(\text{Et}\text{xan})_3$ (table II).

Unfortunately, only one d-d transition is observed in the spectra of the $\text{Co}(\text{bi})_2\text{L}^{-2}$ and $\text{Co}(\text{bi})\text{L}_2^-$ complex ions (table II), so no calculations could be performed.

EXPERIMENTAL

The PMR spectra were recorded with a Varian HA-100 spectrometer operating at 100 MHz. As external reference HMDS was used. The IR data were obtained using a Perkin-Elmer 157 spectrophotometer. UV-VIS spectra were measured with the Cary 14 spectrometer. Magnetic measurements were performed according to the Gouy method.

For preparation of $\text{KCo}(\text{bi})_2$ (8), $\text{Co}(\text{Et}_2\text{dtc})_3$ (9) and $\text{Co}(\text{Et}\text{xan})_3$ (10), the procedures given in the literature were used.

$\text{K}_2\text{Co}(\text{bi})_2(\text{Et}_2\text{dtc}) \cdot 3 \text{H}_2\text{O}$.

To a stirred suspension of $\text{KCo}(\text{bi})_2$ (1 mole) in an ethanol-water mixture (1:1) a solution of $\text{K}(\text{Et}_2\text{dtc})$ (1 mole) in the same solvent was added. The reaction temperature had to be kept at 0° . After half an hour the solution is filtered and on cooling to -5° blue-violet crystals slowly separated. Upon heating the product decomposed near 130° .

Found: Co 11.0; C 19.4; H 3.9; N 17.4; S 11.6. Calc. for $\text{K}_2\text{CoC}_9\text{H}_{22}\text{O}_3\text{N}_7\text{S}_2$ (541.6): Co 10.9; C 20.0; H 4.1; N 18.1; S 11.8.

$\text{NBu}_4\text{Co}(\text{bi})(\text{Bu}_2\text{dtc})_2$.

Two moles of $\text{Na}(\text{Bu}_2\text{dtc})$ were added to a suspension of $\text{KCo}(\text{bi})_2$ (1 mole) in water. After the color of the solution had changed from blue-violet to green, an excess of NBu_4Br was added resulting in the precipitation of a green solid substance. This precipitate was filtered off and purified by dissolving in CHCl_3 and reprecipitation with petroleum ether ($40-60^\circ$). The crystals thus obtained melted at $138-140^\circ$.

Found: Co 7.4; C 50.9; H 9.1; N 10.3. Calc. for $\text{CoC}_{36}\text{H}_{75}\text{N}_6\text{O}_2\text{S}_4$ (811.2): Co 7.3; C 53.3; H 9.3; N 10.3.

$\text{Co}(\text{Et}x\text{an})(\text{Et}_2\text{dtc})_2$.

Two moles of $\text{Co}(\text{Et}_2\text{dtc})_3$ and one mole of $\text{Co}(\text{Et}x\text{an})_3$ were refluxed for 10 minutes in a chloroform solution. The solvent was evaporated and the separated green crystals melted at $131-132^\circ$.

Found: Co 12.5; C 33.6; H 5.4; N 6.2. Calc. for $\text{CoC}_{13}\text{H}_{25}\text{N}_2\text{OS}_6$ (462.2): Co 12.7; C 33.8; H 5.5; N 6.1.

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