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A Novel Type of Penta-Coordinated Iron(III) Complex $FeCl[SSeCNR_2]_2$ ($R=CH_3$, C_2H_5)

Shunji NAKAJIMA and Toshio TANAKA

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-kami, Suita, Osaka 565

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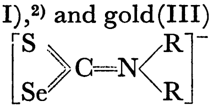
Synopsis. The titled compounds were prepared, and the magnetic susceptibility and electronic spectrum were measured; the two weak bands observed in the near-infrared region are assigned as spin-forbidden d-d bands.

We have previously reported on some *N*,*N*-dialkylthioselenocarbamate complexes of tin(IV),[1] nickel(II), palladium(II), platinum(II),[2] and gold(III),[3] in which the thioselenocarbamate,  ($R=CH_3$, C_2H_5), coordinates through both the sulfur and selenium atoms. Recently, Heber *et al.*[4] prepared a variety of metal *N*,*N*-diethylthioselenocarbamates by the reaction of metal ions with $(C_2H_5)_2NH_2\cdot SSeCN(C_2H_5)_2$.

Our recent study has shown that the reaction of $FeCl_3$ with dimethylchlorotin(IV) *N*,*N*-dialkylthioselenocarbamate, $(CH_3)_2ClSn[SSeCNR_2]$ ($R=CH_3$ and C_2H_5), gave a novel type of penta-coordinate complex, $FeCl[SSeCNR_2]_2$. This paper will report the preparation and properties of this complex.

Experimental

Materials. Dimethylchlorotin(IV) *N*,*N*-dimethyl-[1] and *N*,*N*-diethylthioselenocarbamates,[2] $(CH_3)_2ClSn(dmtsc)$ and $(CH_3)_2ClSn(detsc)$ ($dmtsc=SSeCN(CH_3)_2$, $detsc=SSeCN(C_2H_5)_2$), were prepared as has been described elsewhere.

Preparation. An ethanol–ligroin (1:3 vol/vol) solution (20 ml) of $FeCl_3$ (1.2 mmol) was added, drop by drop, into $(CH_3)_2ClSn(dmtsc)$ (3.7 mmol) in an ethanol–ligroin (1:5 vol/vol) mixture (100 ml) on an ice-bath, after which the solution was stirred for a further 30 min at 0 °C. The precipitate thus obtained was washed with chloroform several times and then dried *in vacuo* to give a black powder of $FeCl(dmtsc)_2$ (1.1 mmol) (mp >250 °C).

Found: C, 17.28; H, 3.15; N, 6.80%. Calcd for $C_6H_{12}N_2S_2Se_2ClFe$: C, 16.93; H, 2.81; N, 6.58%. ν(C=N) 1551 cm^{-1} and μ^{eff} 4.00 BM.

$FeCl(detsc)_2$ was similarly prepared by the reaction of $FeCl_3$ (6.2 mmol) with $(CH_3)_2ClSn(detsc)$ (12—18 mmol). Recrystallization was done from a chloroform–ethanol mixture to give black crystals (3.0 mmol) (mp ~240 °C (decomp.)).

Found: C, 24.66; H, 4.36; N, 5.73%, mol wt, 487 in $CHCl_3$ by a vapor-pressure osmometer. Calcd for $C_{10}H_{20}N_2S_2Se_2ClFe$: C, 24.93; H, 4.19; N, 5.82%; mol wt, 482. ν(C=N) 1509 cm^{-1} and μ^{eff} 3.90 BM.

Physical Measurements. Magnetic susceptibility was measured for micro-crystalline materials by the Gouy method at room temperature. The infrared spectra were recorded in Nujol mulls on a Hitachi-Perkin Elmer 225 spectrophotometer, while the electronic spectra covering the near-infrared region were measured on a Hitachi EPS-03 or 124 spectrophotometer with a 1 cm quartz cell at 25 °C.

Results and Discussion

The reaction of $FeCl_3$ with $(CH_3)_2ClSn(dmtsc)$ or its *N*,*N*-diethyl derivative at the mole ratio of 1:3 was carried out with a view to obtaining $Fe(dmtsc)_3$ or $Fe(detsc)_3$. We have not, however, been successful in isolating the tris-carbamate complex, even in several reaction conditions differing from that described in the Experimental section, such as at an elevated temperature and with prolonged stirring. Instead, the reaction yielded two complexes of a novel type, $FeCl(dmtsc)_2$ and $FeCl(detsc)_2$. This is in contrast with the results reported by Heber *et al.*,[4] who obtained $Fe(detsc)_3$ by the reaction of the Fe(III) ion with $(C_2H_5)_2NH_2(detsc)$ in a methanol–water mixture.

Both the complexes obtained are somewhat sensitive to humidity in air. Molecular-weight determination indicates that the detsc complex is essentially monomeric in chloroform; the dmtsc complex is not sufficiently soluble in common organic solvents to determine the molecular weight.

The magnetic moments of the dmtsc and detsc complexes indicate the presence of three unpaired electrons. This may be compared with the results reported for halogenoiron(III) bis(*N*,*N*-dialkyldithiocarbamate), $FeX[S_2CNR_2]_2$ ($X=Cl$, $R=CH_3$, C_2H_5, and *sec*-C_4H_9; $X=Br$ and I, $R=C_2H_5$),[5] the chloroiron(III) *N*,*N*-diethyl derivative of which has been reported to have an approximate square pyramidal structure, with the iron atom lying above the basal plane formed by the four sulfur atoms.[6] The electronic configuration suggested for these dithiocarbamates, $[(3d_{xy})^2(3d_{xz}3d_{yz})^2(3d_{z^2})^1(3d_{x^2-y^2})^0]$,[5] will be found in $FeCl(dmtsc)_2$ and $FeCl(detsc)_2$.

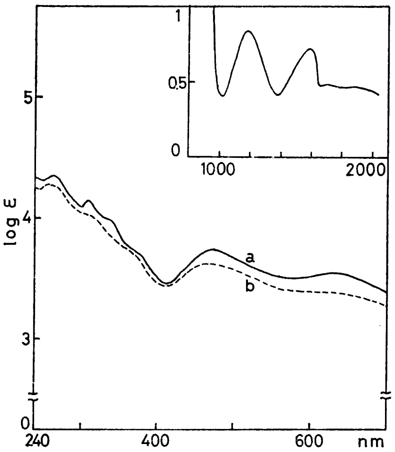


Fig. 1. Electronic spectra of $FeCl(detsc)_2$ (a) and $FeCl(dmtsc)_2$ (b) in dichloromethane.

TABLE 1. ELECTRONIC SPECTRA IN DICHLOROMETHANE; BAND MAXIMA (kK) AND log ε (in parenthesis)

Complex	d-d band	CT band	Ligand band
$FeCl(dmtsc)_2$	16.0 (3.39)	26.5 (3.76)	32.3 (4.04)
	21.4 (3.62)	28.5 (3.82)	38.5 (4.27)
$FeCl(detsc)_2$	6.25 (0.72)	26.6 (3.72)	32.3 (4.14)
	8.40 (0.83)	29.9 (4.01)	37.6 (4.36)
	15.6 (3.54)		
	21.1 (3.75)		

Figure 1 depicts the electronic spectra of the Fe(III) complexes, while the data are listed in Table 1. The spectrum of $FeCl(detsc)_2$ is rich in absorption band and in appearance resembles the spectrum of $FeCl[S_2CN(C_2H_5)_2]$.⁵⁾ The bands observed above 25 kK have their origin in charge-transfer and intra-ligand transitions, while the two succeeding bands at around 21 and 16 kK arise from spin-allowed d-d transitions. These assignments seem reasonable in view of the fact that the bands around 20 and 16 kK of $M(detsc)_n$ (n=3 when M=Cr(III) and Co(III); n=2 when M=Ni(II)) have been identified as d-d transitions,⁴⁾ while the 15.9 kK band⁷⁾ of $Cu(detsc)_2$ is missing.⁴⁾ Moreover, the corresponding dmtsc complexes exhibit similar spectra.⁷⁾ There is, however, little information about the d-d bands of square pyramidal complexes,⁸⁾ and we have to await further studies of this type of complexes before we can make detailed assignments. It is noticed that there are two weak bands of $FeCl(detsc)_2$ in the near-infrared region. In view of the ε values, they are most likely to be spin-forbidden d-d bands, while the analogous weak bands of $FeCl[S_2CN(C_2H_5)_2]_2$ have been assigned as spin-allowed transitions.⁵⁾ No corresponding absorption has been observed in $FeCl(dmtsc)_2$, because of its limited solubility.

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