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Spectral and Magnetic Properties of Some Thioacetamide Complexes of Co^{II} and Ni^{II} [1]

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Received June 28, 1971

Electronic structure parameters and magnetic susceptibilities of tetrahedral Co^{II} complexes of thioacetamide (tac) have been reported. Tentative assignments of the bands in the diffuse reflectance spectra of octahedral and square planar complexes of Ni^{II} with tac have also been made.

Introduction

Thioacetamide has been well known over the years as an analytical reagent but its importance as a sulfur donor ligand has been recognised only recently. Nardelli, *et al.*,[2,3] first prepared several complexes of thioacetamide (tac) of the type $Mtac_2Cl_2$ (M = Fe, Co, Zn, and Cd), $Mtac_4Cl_2$ (M = Ni and Cd), and $Mtac_2(NCS)_2$ (M = Co, Ni, Zn, and Cd) and published crystallographic data on some of these compounds. A complete crystal structure analysis has been made on $Cutac_4Cl_2$ by Truter and Rutherford[4] which showed that Cu^{I} is tetrahedrally bonded to the sulfur atoms of the ligand molecules. Recently Flint and Goodgame[5] from spectral measurements in the infrared and visible regions suggested that the halogeno complexes of thioacetamide with Fe, Co, Zn, and Cd are tetrahedral, the Ni chloro complex is distorted octahedral and the other Ni complexes are square planar. The trans octahedral structure of $Nitac_4Cl_2$ has since then been proved by O'Connor and Amma[6] from crystal structure analysis.

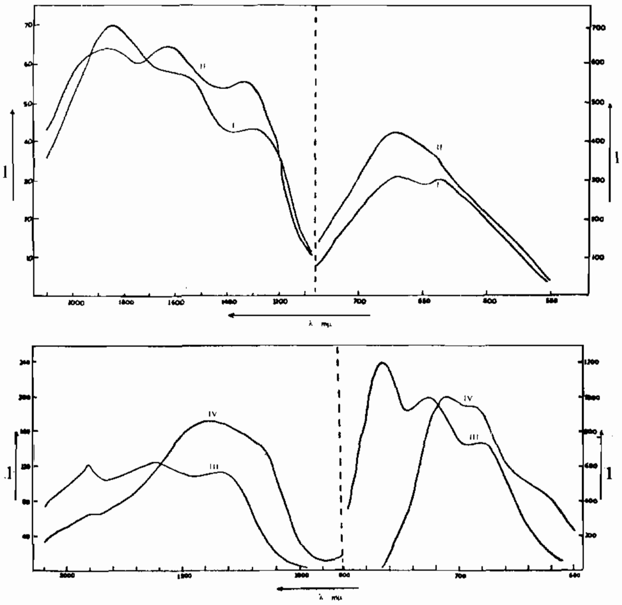
In the following further information on the magnetic and spectral properties of Co^{II} and Ni^{II} complexes of thioacetamide has been presented. While the results obtained generally agree with the previous observations some additional data as reported in this paper seem to warrant publication.

Experimental Section

$Cotac_2Cl_2$, $Cotac_2Br_2$, $Cotac_2I_2$, $Nitac_4Cl_2$, $Nitac_4Br_2$, $Nitac_4I_2$, $Nitac_4(NO_3)_2$, and $Nitac_4(ClO_4)_2$ were prepared by methods same as those used by Flint and Goodgame.[5] All attempts to isolate $Cotac_4(ClO_4)_2$ in the solid state failed. Also $Cotac_2I_2$ was obtained in slightly impure condition. (However, spectra of both compounds were studied in acetone solution of a mixture of the metal salts and an excess of thioacetamide as discussed below.)

Spectral Measurements. Spectra of the cobalt complexes were all measured in acetone solution using a Cary Model 14 recording spectro-photometer. Reflectance spectra of the chloride and bromide complexes of Co were also recorded on the reflectance attachment of Cary 14, $MgCO_3$ being used as standard. Good agreement was obtained between the solution and reflectance spectra of the cobalt complexes. No attempt was made to measure the solution spectra of the Ni complexes because of the uncertainties arising from interaction with solvents. Therefore, all discussions on the spectra of the Ni complexes will be based on their reflectance spectra.

Magnetic Susceptibility Measurements. These measurements were done on a Fonor-type vibrating sample magnetometer manufactured by Princeton ap-



Figures 1. and 2. Spectra of Co^{II} thioacetamide complexes in acetone. I is $Co(tac)_2Cl_2$, II is $Co(tac)_2Br_2$, III is $Co(tac)_2I_2$ and IV is $Cotac_4(ClO_4)_2$ where tac = thioacetamde

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[1] Presented in part at the 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Georgia, November, 1967.
[2] M. Nardelli and I. Chierici, *Gazz. Chim. Ital.*, 1957, *87*, 1478; *ibid.*, *88*, 359 (1958).
[3] M. Nardelli, G.F. Gasperri, A. Mussatti, and A. Manfredotti, *Acta Cryst.*, *21*, 910 (1966).
[4] M.R. Truter and K.W. Rutherford, *J. Chem. Soc.*, 1748 (1962).
[5] C.D. Flint and M. Goodgame, *J. Chem. Soc.* (A), 850 (1968).
[6] J.E. O'Connor and E.L. Amma (private communication).

Table I. Summary of Spectral Assignments and electronic Structure Parameters « Tetrahedral » Co^{II} Complexes v

Compound	$^4A_2 \rightarrow ^4T_1(F)$ $\nu_2 cm^{-1}$	$^4A_2 \rightarrow ^4T_1(P)$ $\nu_3 cm^{-1}$	$D_q cm^{-1}$	$B' cm^{-1}$	β
$Co(Tac)_2Cl_2$	6060	15360	348	731	0.75
$Co(Tac)_2Br_2$	5950	15040	342	715	0.73
$Co(Tac)_2I_2$	6030	13740	349	618	0.63
$Co(Tac)_4(ClO_4)_2$	7170	14600	420	610	0.62
$Co(tu)_4(ClO_4)_2$	7200	14500	425	600	0.62

B for gaseous Co^{2+} ion = 976 cm^{-1}; B = B'/976.

Table II. Magnetic Data on Co^{II} and Ni^{II} Thioacetamide Complexes at 300 K

	Dia. Corr. × 10^6	T.I.P. × 10^6	M. Corr. × 10^6 C.G.S.U.	μB.M.
$Co(tac)_2$	154.9	600	8995	4.64
$Co(tac)_2Br_2$	177.3	611	8991	4.64
$Ni(tac)_4Cl_2$	250.2	243	4178	3.17
$Ni(tac)_4Br_2$				
$Ni(tac)_4I_2$				
$Ni(tac)_4(NO_3)_2$		Diamagnetic		
$Ni(tac)_4(ClO_4)_2$				

plied research on a twelve inch varian magnet. The magnetometer was calibrated with a nickel standard and $Co[Hg(NCS)_4]$. The susceptibilities were corrected for diamagnetism and temperature independent paramagnetism.

Results and Discussion

Cobalt Complexes. The spectra of the cobalt complexes in acetone solution are represented in Figure 1 and Figure 2 and the asisgnments and numerical values of pertinent quantities are tabulated in Table I. The magnetic susceptibility data are listed in Table II.

The shape and high intensities of the absorption bands in the visible and near infrared as well as the magnetic moments (4.5 B.M.) clearly indicate a tetrahedral stereochemistry for Co^{II} in these complexes. Since the spectra of these compounds is very similar to those of the analogous thiourea complexes, it is expected that these are sulfur bonded as are all clearly established thiourea complexes.[7-19]

Selection of single energy values for the transitions $^4A_2 \rightarrow ^4T_1(F)$ and $^4A_2 \rightarrow ^4T_1(P)$ has been made by visual estimation of the center of gravity of the band. The values of D_q and B' were calculated from ν_2 and ν_3 by solving the appropriate Tanabe and Sugano matrices.[20] The D_q, B', and β values in Table I are very similar to those found for thiourea (tu)[21] and ethylene thiourea (etu)[22] complexes. Hence thioacetamide occupies approximately the same position as thiourea in the spectrochemical and nephelauxetic series, *i.e.* a weak field ligand that brings about a substantial reduction of the electrostatic repulsion parameters.

Nickel Complexes. The reflectance spectra of the various Ni^{II} thioacetamide complexes studied are shown in Figure 3 and the assignments for these bands are enumerated in Table III. A resume of the room temperature magnetic susceptibilities is found in Table II. The color (green), spectra and magnetic moment (3.12 B.M.) of $Ni(tac)_4Cl_2$ places this complex in a class by itself. The reflectance spectra is very similar to that found by Hare and Ballhausen[23] for $Nitu_6Cl_2$. They have interpreted the spectra of $Nitu_6$-

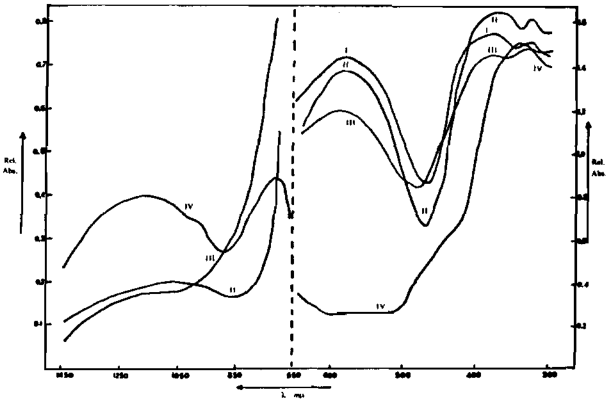

Figure 3. Diffuse reflectance spectra of solid Ni^{II} thioacetamide complexes. I is $Ni(tac)_4(NO_3)_2$, II is $Ni(tac)_4(ClO_4)_2$ III is $Ni(tac)_4Br_2$ and IV is $Ni(tac)_4Cl_2$.

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Table III. Assignments of Spectral Bands for $Ni(Tac)_4Cl_2$

νcm^{-1}	νcm^{-1}	νcm^{-1}	νcm^{-1}	νcm^{-1}
$^{3}B \rightarrow \begin{matrix} ^{3}B \\ ^{3}E \end{matrix}$	$^{3}B \rightarrow \begin{matrix} ^{1}A(^{1}Eg) \\ ^{1}B \end{matrix}$	$^{3}B \rightarrow \begin{matrix} ^{3}A \\ ^{3}E \end{matrix}$	$^{3}B \rightarrow \begin{matrix} ^{1}B(^{1}T_{2g}) \\ ^{1}E \end{matrix}$	$^{3}B \rightarrow {}^{3}A$
8700	10260	13890	17860	21280

Assignments of Spectral Bands for Planar Complexes of Ni

	$\nu_1 cm^{-1}$ $^{1}A_{1g} \rightarrow {}^{3}B_{1g}$	$\nu_2 cm^{-1}$ $^{1}A_{1g} \rightarrow {}^{1}B_{1g}$	$\nu_3 cm^{-1}$
$Ni(tac)_4Br_2$	9090	17094	29850 26310
$Ni(tac)_4I_2$	11100	16390	29850 26670
$Ni(tac)_4(NO_3)_2$	9302	17240	30300 26310
$Ni(tac)_4(ClO_4)_2$	9940	17390	30770 27030

Cl_2 based upon a weak tetragonal distortion of the octahedral field model. The asignments of Table III follow theirs. The magnetic moment of $Nitac_4Cl_2$ is also very similar to $Ni(tu)_4Cl_2$. However, $Nitac_4Cl_2$ is not related in any simple way to $Nitu_4Cl_2$ crystallographically and is not isostructural.[6]

On the other hand the compounds $Nitac_4X_2$ where X is Br^-, I^-, ClO_4^-, and NO_3^- all of which are blue and diamagnetic are most conceivably square planar. The diffuse reflectance spectra of these compounds have been interpreted on this basis. A tentative assignment of transitions following the strong field approximation of Ballhausen and Liehr[24] is indicated in Table III. Except for the iodide derivative ν_1 and ν_2 are separated by approximately 8000 cm^{-1} which is comparable to the value obtained from the energy expressions of Ballhausen and Leihr.[24] Hence, the band at 11000 Å is assigned to the $^{1}A_{1g} \rightarrow {}^{3}B_{1g}$ transition and the band at 5500 Å is assigned to the $^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transition. A third high energy band ($^{1}A_{1g} \rightarrow {}^{1}A_{1g}$) expected to occur at 50,000 cm^{-1} is possibly obscured by intense charge transfer bands which begin at 20,000 cm^{-1} (5000 Å).

Acknowledgment. The author wishes to thank Dr. E. L. Amma and Dr. E. L. Jones, Jr. of the Chemistry and Physics departments of the University of South Carolina, Columbia, South Carolina, for help received in spectral and magnetic measurements.

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