

Complexes of Pyridine-2-carbaldehyde *S*-Methylthiosemicarbazone with Nickel(II) and Copper(II)

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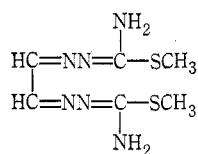
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Abstract

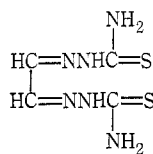
New complexes of pyridine-2-carbaldehyde *S*-methylthiosemicarbazone (pmts) with nickel(II) and copper(II) are reported, together with magnetic moments, infrared and electronic spectra. The pale yellow bis-ligand complexes with nickel perchlorate, tetrafluoroborate and nitrate have the ionic structures $[\text{Ni}(\text{pmts})_2] \text{X}_2$, with six-coordinate nickel(II) and tridentate ligands. Thiocyanate coordination and bidentate pmts appear to be present in the six-coordinate orange-brown complex $\text{Ni}(\text{pmts})_2(\text{NCS})_2$. The complexes, $\text{Ni}(\text{pmts})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}$), are halogen-bridged and six-coordinate. The complexes $\text{Cu}(\text{pmts})\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$) do not appear to be five-coordinate, and may be six-coordinate.

Introduction

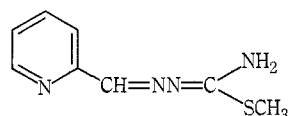
The Schiff base (1) of *S*-methylthiosemicarbazide with glyoxal was found¹ to have a much lower antitumour activity than the corresponding Schiff base (2) of thiosemicarbazide. This was attributed to the poorer donor properties of (1) caused by



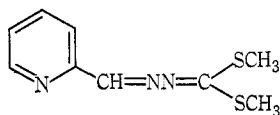
(1)



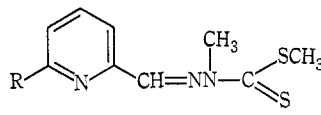
(2)



(3)



(4)



(5) $\text{R} = \text{H}$

(6) $\text{R} = \text{CH}_3$

S-alkylation, which prevents inner complex formation.^{1,2} No complexes of (1) appear to have been isolated. We find that the Schiff base of *S*-methylthiosemicarbazide with pyridine-2-carbaldehyde, (3) (pmts), yields stable nickel and copper complexes. These appear to be the first complexes reported with Schiff bases of *S*-methylthiosemi-

¹ French, F. A., and Freedlander, B. L., *Cancer Res.*, 1958, **18**, 1290.

² Bähr, G., and Schleitzer, G., *Z. Anorg. Allg. Chem.*, 1955, **280**, 161.

carbazine of the type $RR'C=NN=C(NH_2)SMe$, in contrast to the wide range obtained with Schiff bases of thiosemicarbazide.^{3,4}

Results and Discussion

The complexes (Table 1) were all obtained readily from ethanolic solutions and the nickel compounds are high-spin. The bis-ligand nickel perchlorate, tetrafluoroborate and nitrate complexes appear to have the ionic structures $[Ni(pmts)_2] X_2$ ($X = ClO_4$, BF_4 , NO_3) on the basis of the conductivity of the perchlorate (Table 1, footnote^B), the infrared absorption at $c. 1340\text{--}50\text{ cm}^{-1}$ assigned to ionic nitrate, and the broad absorptions at $c. 1100\text{ cm}^{-1}$ associated with ionic tetrafluoroborate and perchlorate.⁵ These complexes have similar electronic spectra (Table 1) typical of pseudo-octahedral nickel(II) with a symmetric band $c. 12200\text{ cm}^{-1}$ and a shoulder $c. 18200\text{ cm}^{-1}$ attributed to the transitions ${}^3T_{2g} \leftarrow {}^3A_{2g} (v_1)$ and ${}^3T_{1g}(F) \leftarrow {}^3A_{2g} (v_2)$ of nickel(II) (O_h symmetry).⁶ This suggests that the *pmts* ligands are tridentate. The spectra are similar to the spectra of other $[NiL_2]^{2+}$ cations with the related NNS donors (4) and (5) which contain donor thioether or thioketone sulphurs.^{7,8} This is consistent with sulphur coordination by tridentate *pmts* molecules.

The electronic spectrum of $Ni(pmts)_2(NCS)_2$ indicates a six-coordinate structure. This orange-brown complex has a $10Dq (v_1)$ value of $11100 \pm 100\text{ cm}^{-1}$, outside the range of $12100\text{--}12700\text{ cm}^{-1}$ for the yellow complexes $[Ni(pmts)_2] X_2$ ($X = ClO_4$, BF_4 , NO_3) and similar complexes with the related NNS ligands (4) and (5).^{7,8} This suggests that the simple $[Ni(pmts)_2]^{2+}$ cation may not be present in $[Ni(pmts)_2(NCS)_2]$. Anion infrared absorption occurs at 820 cm^{-1} , indicating *N*-bonded thiocyanate; the 750 cm^{-1} region, in which ionic thiocyanate absorbs, was obscured and no anion bands could be assigned in the $440\text{--}490\text{ cm}^{-1}$ region. Three sharp bands occur at 2080 , 2060 and 2030 cm^{-1} in the range for *N*-bonded and ionic thiocyanate,⁵ suggesting that the two thiocyanate groups are in different environments. We propose that one or both thiocyanates are coordinated, with one or both ligand molecules bidentate, presumably NN-bonded. Conductivity measurements could not be performed because of the low solubility of the complex in suitable solvents. Similar NN and NNS coordination is found with (4) which like *pmts* has a weakly coordinating thioether group,⁷ whereas exclusively NNS bonding is found for (5), (6) and pyridine-2-carbaldehyde thiosemicarbazone, which contain thioketone groups.^{4,8,9}

The spectra of the halide complexes $Ni(pmts)X_2$ resemble those for distorted six-coordinate nickel(II) complexes, with components of v_1 and v_2 probably being present^{6,8} (Table 1). The complexes presumably have halogen-bridged six-coordinate structures with the unsymmetrical chromophore NiN_2SX_3 .

The spectra of copper halide complexes with *pmts* and (5) have a smooth band at $13000\text{--}14000\text{ cm}^{-1}$. The ligand (6), which has a 2-methyl-substituted pyridine, yields

³ Ablov, A. V., and Gerbeleu, N. V., and Shopron, M. V., *Russ. J. Inorg. Chem.*, 1971, **16**, 932, and previous papers by the first two workers.

⁴ Ablov, A. V., and Belichuk, N. I., *Russ. J. Inorg. Chem.*, 1969, **14**, 93.

⁵ Nakamoto, K., 'Infrared Spectra of Inorganic and Coordination Compounds' (John Wiley: New York 1970).

⁶ Lever, A. B. P., 'Inorganic Electronic Spectroscopy' (Elsevier: Amsterdam 1968).

⁷ Akbar Ali, M., Livingstone, S. E., and Phillips, D. J., *Inorg. Chim. Acta*, 1972, **6**, 552.

⁸ Akbar Ali, M., Livingstone, S. E., and Phillips, D. J., *Inorg. Chim. Acta*, 1972, **6**, 11.

⁹ Akbar Ali, M., Livingstone, S. E., and Phillips, D. J., *Inorg. Chim. Acta*, 1972, **6**, 39.

five-coordinate copper halide complexes⁹ with spectra containing a broad band centred at 10500 cm^{-1} and shoulders at $c. 9000\text{ cm}^{-1}$ and $c. 12000\text{ cm}^{-1}$. The pmts copper complexes do not appear to be five-coordinate and may be six-coordinate, with bridging halide. The complex $\text{Cu(pmts)(NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ has infrared absorptions at $c. 1450$, $c. 1300\text{ cm}^{-1}$ (both superimposed on ligand bands) and 1020 cm^{-1} assigned to coordinated nitrate. No absorption at $c. 1350\text{ cm}^{-1}$ could be detected for ionic nitrate and in view of its prominence in $[\text{Ni(pmts)}_2][\text{NO}_3]_2 \cdot \text{H}_2\text{O}$ we assume that both nitrates are coordinated in $\text{Cu(pmts)(NO}_3)_2$. Attempts to isolate pure cobalt(II) complexes with pmts were unsuccessful.

Table 1. Magnetic moments and diffuse reflectance spectra

All complexes were analysed for C, H, N and metal, and some for S. Satisfactory analyses were obtained in each case.^A All spectra contained strong ligand and charge-transfer absorption extending from $c. 20000\text{ cm}^{-1}$ to higher frequencies

Complex formula	Colour	μ_{eff} (B.M.)	$10^{-3}\nu_{\text{max}}$ [cm^{-1} ; shoulders in <i>italics</i> (approx. values)]			
Ni(pmts)Cl_2	pale green	3.04	8.0	12.0br	13.5w	16.0
Ni(pmts)Br_2	pale green	3.10	7.7	11.0w	12.5br	13.7w 15.2
$[\text{Ni(pmts)}_2][\text{ClO}_4]_2 \cdot \frac{1}{2}\text{EtOH}^B$	pale yellow	3.15	12.1	18.2		
$[\text{Ni(pmts)}_2][\text{BF}_4]_2$	pale yellow	3.16	12.3	18.5		
$[\text{Ni(pmts)}_2][\text{NO}_3]_2 \cdot \text{H}_2\text{O}$	pale yellow	3.11	12.2	18.0		
$\text{Ni(pmts)}_2(\text{NCS})_2$	orange-brown	3.07	11.1	16.0		
Cu(pmts)Cl_2	pale green	1.88	13.3			
Cu(pmts)Br_2	pale green	1.85	13.5			
$\text{Cu(pmts)(NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$	green	1.88	13.7			

^A Data may be obtained on application to the Editor-in-Chief, Editorial and Publications Service, CSIRO, 372 Albert Street, East Melbourne, Vic. 3002.

^B The molecular conductivity in 10^{-3}M MeNO_2 at 25° is $179\text{ S cm}^2\text{ mol}^{-1}$.

Experimental

Pyridine-2-carbaldehyde *S*-Methylthiosemicarbazone (3) (pmts)

Pyridine-2-carbaldehyde (13.8 g) was added to a solution of *S*-methylthiosemicarbazide hydrogen iodide, $\text{NH}_2\text{N}=\text{C}(\text{NH}_2)\text{SMe}\cdot\text{HI}$,¹⁰ (30 g) in ethanol (60 ml). After the solution was cooled, yellow crystals of pyridine-2-carbaldehyde *S*-methylthiosemicarbazone hydrogen iodide, $\text{C}_5\text{H}_4\text{NCH}=\text{NN}=\text{C}(\text{NH}_2)\text{SMe}\cdot\text{HI}$, separated; yield 80% and m.p. 160°C . When aqueous solutions of $\text{C}_5\text{H}_4\text{NCH}=\text{NN}=\text{C}(\text{NH}_2)\text{SMe}\cdot\text{HI}$ were treated with the equimolar amount of aqueous potassium hydroxide, and the solution then cooled in ice, yellow crystals of pyridine-2-carbaldehyde *S*-methylthiosemicarbazone (3) were deposited. The crystals were washed thoroughly with water and dried under vacuum; yield 45% and m.p. 108°C .

Metal Complexes of pmts

These were deposited after mixing alcoholic solutions of pmts and metal salt in the appropriate proportions. The complexes were filtered off, washed with ethanol and ligroin, and dried under vacuum.

Analyses and Physical Measurements

These were as previously described.⁷⁻⁹

Manuscript received 30 October 1973

¹⁰ Freund, M., and Paradies, T., *Ber. Deut. Chem. Ges.*, 1901, **34**, 3113.