

PREPARATION AND CHARACTERIZATION OF INDANE-1,2,3-TRIONE MONOTHIOSEMICARBAZONE COMPLEXES WITH Cu(II), Pd(II), Ag(I), Cd(II), Hg(II) AND Pb(II)

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ABSTRACT

Complexes of indane-1,2,3-trione monothiosemicarbazone with several heavy metal ions have been isolated and characterized. Structures have been assigned to these complexes based on electrical conductivity, magnetic susceptibility, infrared and electronic spectral data.

INTRODUCTION

THE present heightened interest in the chemistry of thiosemicarbazones stems from their biological activity¹. They have also been long known for their versatile chelating ability and many chelates have been reported². However, structural studies on heavy metal complexes of thiosemicarbazone are scarce. The earlier studies on metal complexes of indane-1,2,3-trione monothiosemicarbazone (ITMT) were carried out in solution phase and were concerned with the possible use of ITMT for the spectrophotometric determination of copper³, palladium³ and osmium⁴. Structural studies on metal derivatives of ITMT, however, have not been carried out so far.

EXPERIMENTAL

Materials

Indane-1,2,3-trione monothiosemicarbazone was prepared as described earlier⁴. ITMT solution (1×10^{-2} M) was prepared in dimethylformamide (DMF).

Preparation of the complexes

The complexes with Cu(II), Pd(II), Ag(I), Cd(II), Hg(II) and Pb(II) were prepared by adding a hot aqueous solution of the respective metal chloride or nitrate dropwise to a boiling solution of the ligand containing sodium acetate (1 g) until the metal-to-ligand ratio reached 1:2. The solid that separated was filtered, washed with hot water and ethanol, and dried in an electric oven at 90°C.

Physical methods of analysis

Molar conductances of the complexes in DMF ($Ca\ 10^{-3}$ M) were determined at $29 \pm 2^\circ\text{C}$ using a

Systronics 303 direct reading conductivity bridge. Magnetic susceptibility was measured by the Guoy method at room temperature. The electronic spectra were recorded on a Carl Zeiss DMR-21 spectrophotometer. The IR spectra were recorded in the range $4000-180\text{ cm}^{-1}$ on a Perkin Elmer 983 G IR spectrophotometer in KBr medium.

RESULTS AND DISCUSSION

The analytical data (table 1) show that the complexes have the formula $M(\text{ITMT})_2\text{Cl}_2$ (where $M = \text{Cu, Pd, Hg, Cd}$), $\text{Ag}(\text{ITMT})_2\text{NO}_3$ and $\text{Pb}(\text{ITMT})_2(\text{NO}_3)_2$.

Electrical conductance

The molar conductance (Λ_M) values (given in parentheses) in DMF for $\text{Cu}(\text{ITMT})_2\text{Cl}_2$ (80), $\text{Pd}(\text{ITMT})_2\text{Cl}_2$ (80), $\text{Ag}(\text{ITMT})_2\text{NO}_3$ (60), $\text{Cd}(\text{ITMT})_2\text{Cl}_2$ (90), $\text{Hg}(\text{ITMT})_2\text{Cl}_2$ (120) and $\text{Pb}(\text{ITMT})_2(\text{NO}_3)_2$ (125) suggest the 1:1 electrolytic nature of the silver complex and 1:2 electrolytic nature of the copper, palladium, cadmium, mercury and lead complexes.

Magnetic properties

The Cu(II) complex gives a magnetic moment (μ_{eff}) of 1.81 which is very close to spin only for one unpaired electron. It is in the region normally observed for Cu(II) complexes having an orbitally non-degenerate B_{1g} ground state, indicating no metal-metal interaction⁵. The diamagnetism of Pd(II), Cd(II), Hg(II) and Pb(II) complexes suggests square planar environment around the metal ions (table 2).

Infrared spectra

The IR spectra of the ligand and the complexes were examined in detail. The highest frequency

Table 1 Analytical data for 1,2,3-trione monothiosemicarbazone complexes*

Complex	% Carbon	% Hydrogen	% Nitrogen	% Chlorine	% Metal
Cu(ITMT) ₂ Cl ₂	38.75(39.97)	2.15(2.34)	13.95(13.86)	11.25(11.79)	11.20(10.57)
Pd(ITMT) ₂ Cl ₂	37.75(37.31)	2.21(2.19)	13.25(13.05)	11.20(11.01)	16.21(16.52)
Ag(ITMT) ₂ NO ₃	37.60(37.75)	2.10(2.21)	15.25(15.41)	—	15.55(15.41)
Cd(ITMT) ₂ Cl ₂	36.50(36.96)	2.15(2.17)	12.50(12.93)	11.10(10.90)	17.10(17.29)
Hg(ITMT) ₂ Cl ₂	32.10(32.55)	1.95(1.91)	11.50(11.39)	9.50(9.60)	26.90(27.18)
Pb(ITMT) ₂ (NO ₃) ₂	31.50(30.10)	1.75(1.76)	13.90(14.04)	—	26.50(25.96)

*Calculated values are in parentheses.

band of the ligand at 3394 cm^{-1} may be assigned to the asymmetric stretching vibration of the terminal NH_2 group⁶. The other bands at 3251 and 3158 cm^{-1} may be due to the superimposed form of the symmetric $\nu_{(\text{N-H})}$ bands of the amino and imino groups⁷. These bands are not affected in the complexes, which indicates that the terminal $-\text{NH}_2$ does not take part in the coordination. A strong absorption of ITMT at 1136 and 856 cm^{-1} may be assigned to $>\text{C}=\text{S}$ stretching vibration^{8,9}, unaffected in all complexes.

A sharp and strong band at 1686 cm^{-1} in the spectrum of the ligand has been observed and is due to the $\nu_{(\text{C}=\text{N})}$ mode of the azomethine linkage¹⁰. In the complexes this band appears around 1600 cm^{-1} . The downward shift in the position of $\nu_{(\text{C}=\text{N})}$ indicates that the unsaturated nitrogen of the azomethine linkage is coordinated to the metal atom¹¹. Another important band at 1721 cm^{-1} in ITMT is

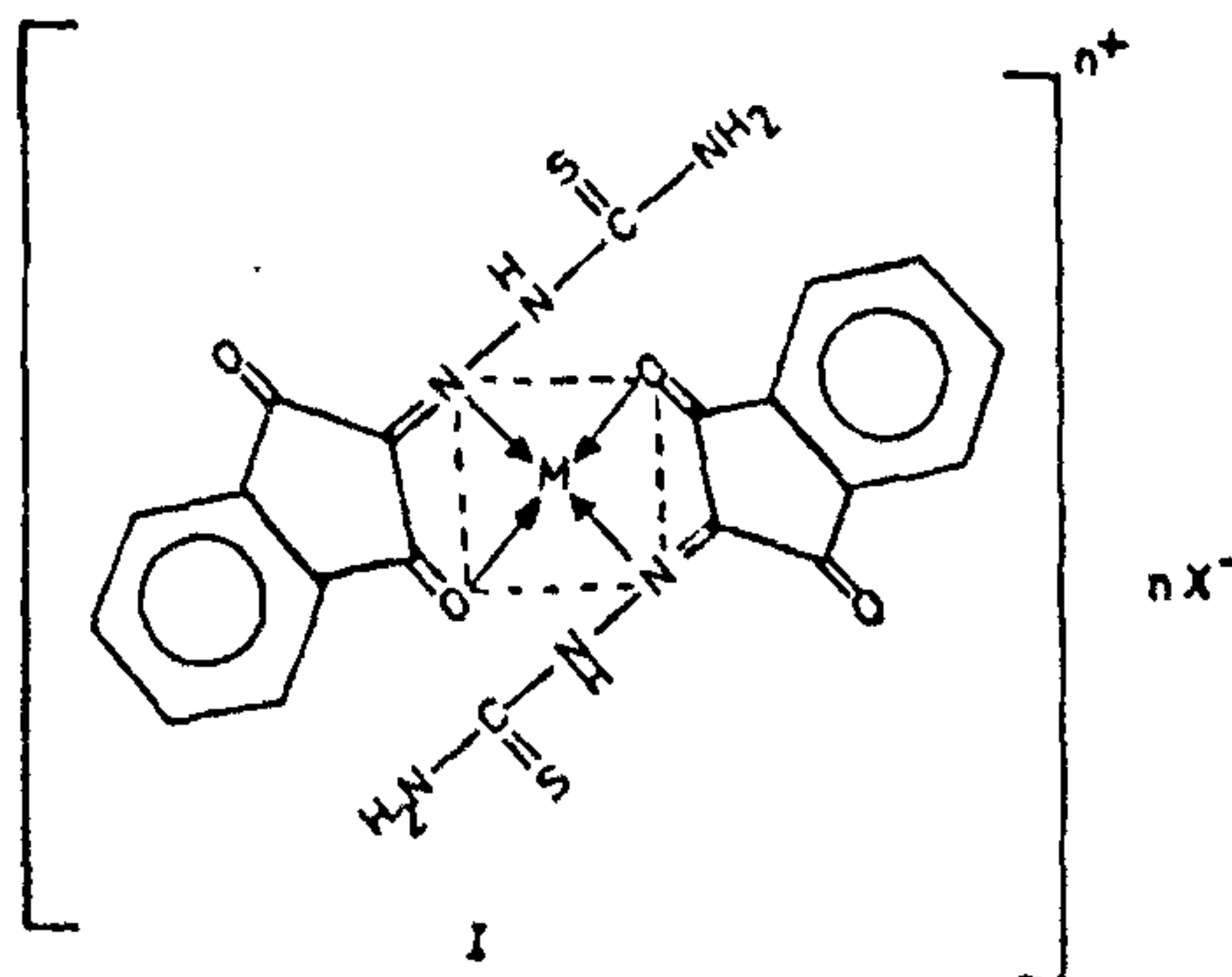
assigned to $\nu_{(\text{C}=\text{O})}$ of the indane ring and its shifting in the complexes indicates the participation of the oxygen ($\text{C}=\text{O}$) atom in chelation in analogy with the previous observation¹². The bands appearing around 510 and 430 cm^{-1} in the spectra of the complexes may be assigned to $\text{M}-\text{N}$ and $\text{M}-\text{O}$ stretching frequencies respectively.

Electronic spectra

The electronic spectrum of the copper complex shows peaks at 23200 and 15500 cm^{-1} . The latter band is assigned to the ${}^2\text{B}_{1g} \rightarrow {}^2\text{B}_{2g}$ transition of square planar Cu(II) by analogy with the spectra of other square planar Cu(II) species. The band observed at 23200 cm^{-1} is attributed to ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_g$ transition. The intense band at 21700 cm^{-1} in the spectrum of the palladium complex, assignable to ${}^1\text{A}_g \rightarrow {}^1\text{B}_{1g}$ transition suggests a square planar structure. The ITMT complexes of Ag, Cd, Hg and Pb presumably have square planar configuration¹³ on the basis of analytical, conductance and IR spectral studies.

Table 2 Magnetic and electronic spectral data of indane 1,2,3-trione monothiosemicarbazone complexes

Complexes	Colour	μ_{eff} (B.M.)	Observed bands (cm^{-1})
Cu(ITMT) ₂ Cl ₂	Yellow	1.81	23200 15500
Pd(ITMT) ₂ Cl ₂	Brown	Diamagnetic	21700
Ag(ITMT) ₂ NO ₃	Brownish-red	Diamagnetic	30300 27000 15150
Hg(ITMT) ₂ Cl ₂	Orange-red	Diamagnetic	29400 27000
Cd(ITMT) ₂ Cl ₂	Deep yellow	Diamagnetic	29850 22700
Pb(ITMT) ₂ (NO ₃) ₂	Red	Diamagnetic	30300 23260



where, n = valence of M
 $X = \text{Cl}, \text{NO}_3$
 $M = \text{Cu}, \text{Pd}, \text{Cd}, \text{Ag}, \text{Hg}, \text{Pb}$

On the basis of the evidence given above, the following structure (I) of the complexes has been proposed.

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NEWS

CAMBRIDGE NEHRU SCHOLARSHIPS 1988

The following ten scientists from different Indian universities and educational establishments have been offered Cambridge Nehru Scholarships this year for postgraduate research at the University of Cambridge: The subject of specialization of each scientist is given in parentheses. 1. Shri Atul Bas-
kar, Indian Institute of Technology, Delhi (Mechanical Engineering), 2. Shri Onkar Dikshit, University of Roorkee, Roorkee (Environmental Geography). 3. Shri M. S. P. Gopal, University of Bombay, Bombay (Soil Mechanics), 4. Miss Dipa Natar-

ajan, University of Madras, Madras, (Genetics), 5. Shri Sukhandu Samajdar, Indian Institute of Science, Bangalore (Materials Sciences), 6. Shri Pulak Sengupta, Jadavpur University, Calcutta (Earth Sciences), 7. Miss Rumina Sethi, Panjab University, (English), 8. Shri Ajay Skaria, M.S. University of Baroda, Baroda, (History), 9. Shri L. S. Shashidhara, University of Agricultural Sciences, Dharwad, (Plant Genetics) and 10. Shri T. A. S. Srinivas, Indian Institute of Technology, Madras (Microelectronics).