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Some Platinum Group Metal Complexes of Substituted Thiosemicarbazones

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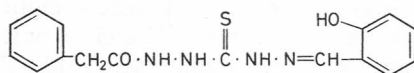
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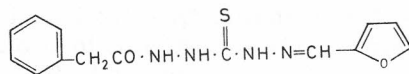
Complexes of Ru(III), Rh(III) and Pt(IV) with 1-salicyl-4-benzylamidothiosemicarbazone (SBTS) and 1-(α -furyl-4-benzylamidothiosemicarbazone (FBTS) have been prepared and their stereochemistry proposed on the basis of magnetic and electronic spectral studies. The ruthenium(III) complexes reveal an anomalous magnetic behaviour which may possibly be attributed to a large spin-orbit coupling. The rhodium(III) and platinum(IV) complexes of SBTS conform to the octahedral geometry. Relevant ligand-field parameters, wherever possible, have been calculated. Infra-red studies indicate the (S, N) bidentate nature of FBTS, whereas SBTS acts as a (S, N, O) tridentate ligand.

INTRODUCTION

Complexes of substituted thiosemicarbazide and their derivatives with a number of transition metals have been studied in our laboratory¹⁻⁴, but relevant data on platinum metal complexes are still scarce. These ligands as well as their metal chelates have added importance on account of their biological activity⁵⁻¹⁰. The present article deals with the preparation and properties of some platinum-group metal complexes of 1-salicyl-4-benzylamidothiosemicarbazone (SBTS) and 1-(α -furyl-4-benzylamidothiosemicarbazone (FBTS).



SBTS



FBTS

RESULTS AND DISCUSSION

Chemical analysis of all the complexes studied suggests a metal-to-ligand stoichiometry of 1 : 2 (see Table I).

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TABLE I
Analytical Data on Platinum Metal Complexes of SBTS and FBTS

| Complex | Colour | | C % | H % | N % | M % | Cl % |
|---|------------------|-------|--------|--------|--------|--------|---------|
| [Ru(C ₁₆ H ₁₅ N ₄ O ₂ S) ₂]Cl·2H ₂ O | Brown | Found | 46.62 | 4.19 | 13.47 | 12.34 | 4.37 |
| | | Calc. | 46.45 | 4.11 | 13.54 | 12.23 | 4.29 |
| [Ru(C ₁₄ H ₁₄ N ₄ O ₂ S) ₂ Cl ₂]Cl·2H ₂ O | greyish brown | Found | 39.45 | 3.59 | 13.8 | 7.65 | 12.03 |
| | | Calc. | 39.65 | 3.78 | 13.22 | 7.55 | 11.03 |
| [Rh(C ₁₆ H ₁₅ N ₄ O ₂ S) ₂]Cl | reddish brown | Found | 48.27 | 3.82 | 14.39 | 12.91 | 4.52 |
| | | Calc. | 48.45 | 3.78 | 14.14 | 13.00 | 4.48 |
| [Rh(C ₁₄ H ₁₄ N ₄ O ₂ S) ₂ Cl ₂]Cl | dark brown | Found | 41.50 | 3.48 | 13.89 | 12.69 | 12.96 |
| | | Calc. | 41.30 | 3.44 | 13.77 | 12.65 | 13.08 |
| [Pt(C ₁₆ H ₁₅ N ₄ O ₂ S) ₂]Cl ₂ | dark pink | Found | 41.87 | 3.19 | 12.30 | 21.41 | 7.67 |
| | | Calc. | 41.73 | 3.26 | 12.18 | 21.20 | 7.72 |
| [Pt(C ₁₄ H ₁₄ N ₄ O ₂ S) ₂]Cl ₂ | pink | Found | 35.83 | 3.05 | 12.02 | 20.59 | 15.15 |
| | | Calc. | 35.71 | 2.97 | 11.90 | 20.73 | 15.07 |

The room-temperature magnetic moments of ruthenium(III) complexes of FBTS and SBTS were observed to be 2.01 and 2.13, respectively, which suggests that the complexes are of the d^5 low-spin type^{11,12}. The spin-orbit coupling for these complexes is expected to be strong; it was evaluated from the magnetic data using the equation given by Kotani¹³ (see Table II). These values of λ are in fair agreement with the values reported earlier for ruthenium(III) complexes^{14,15}; the latter values are suggestive of a slight distortion from the octahedral symmetry which would lead to a similar splitting of the t_{2g} level if combined with the spin-orbit coupling effect. Such a distortion would probably have its origin in the Jahn-Teller effect, but it would be small unless there was a high degree of π -bonding¹⁶. However, electronic spectral data do not point out this distortion, though it is expected on the basis of the spin-orbit coupling and the Jahn-Teller effect. Besides, the unequal field strength in the xy - and z -plane in the case of the $[\text{Ru}(\text{FBTS})_2\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ complex may also be the cause of distortion. The ground term of the ruthenium(III) complex is $^2A_{2g}(t_{2g}^5)$. The Tanabe-Sugano diagram¹⁷ predicts eight transitions from the ground state t_{2g}^5 to the doublet state $t_{2g}^4e_g^1$. The electronic spectra of the present complexes, however, show only five bands (see Table II). The assignments of $d-d$ transitions are rather difficult. The band at $20\,830\text{ cm}^{-1}$ is probably due to the $^2T_{2g} \rightarrow ^2A_{2g}$ transition and the strong highest-energy band ($\sim 33\,900\text{ cm}^{-1}$) may arise owing to the charge transfer from the ligand to the metal. The first and third weak low-energy bands are assigned to two spin-forbidden transitions, the separation between them amounting to $8B$. The magnitude of this separation was useful in evaluating the electronic repulsion parameter B . The value of $10 Dq$ was calculated employing the ratio $Dq/B = 5.1$. The values of these parameters are summarized in Table II.

Both rhodium(III) complexes under investigation were found to be diamagnetic at room temperature ($X_g = -2.458 \times 10^{-6}$ and -2.157×10^{-6} c. g. s. for the SBTS and FBTS complexes, respectively). The spectra of $\text{Rh}(\text{SBTS})_2\text{Cl}$ can be interpreted in terms of the octahedral symmetry, as expected for this complex. The two bands observed can tentatively be assigned¹⁸ to the spin-

TABLE II
Electronic Spectral Data on Platinum Metal Complexes

| Complex | Obs. bands | Assignments | Ligand Field Parameters |
|--|--|---|---|
| [Ru(C ₁₆ H ₁₅ N ₄ O ₂ S) ₂]Cl | 15 940 18,350 20,830 31 750 33,900 | ² T _{2g} → ² A _{2g} Charge Transfer | 10Dq = 31,110 λ = -1,676 B = 610; C = 2 440 |
| [Ru(C ₁₄ H ₁₄ N ₄ O ₂ S) ₂ Cl ₂]Cl | 16 000 18 350 20 620 31,250 33,330 | ² T _{2g} → ² A _{2g} Charge Transfer | 10Dq = 29 450; λ = -1451 B = 577; C = 2 308 |
| [Rh(C ₁₆ H ₁₅ N ₄ O ₂ S) ₂]Cl | 25 640 34 490 | ¹ A _{1g} → ¹ T _{1g} → ¹ T _{2g} | 10Dq = 27 850 B = 553 C = 2 212 |
| [Rh(C ₁₄ H ₁₄ N ₄ O ₂ S) ₂ Cl ₂]Cl | 21 980 25,970 33 900 | ¹ A _{1g} → ¹ E _g → ¹ A _{2g} → ¹ T _{2g} | Dq(E) = 2 498 Dq(A) = 1 700 Dt = 456 |
| [Pt(C ₁₆ H ₁₅ N ₄ O ₂ S) ₂]Cl ₂ | 24 100 31 250 37 740 | ¹ A _{1g} → ³ T _{1g} , ³ T _{2g} → ¹ T _{1g} → ¹ T _{2g} | 10Dq = 33 070 B = 458 C = 1852 |
| [Pt(C ₁₄ H ₁₄ N ₄ O ₂ S) ₂ Cl ₂]Cl ₂ | 24 390 28 370 32 790 37 040 | ¹ A _{1g} → ³ T _{1g} , ³ T _{2g} → ¹ E _g → ¹ E _{2g} → ¹ T _{2g} | Dq(E) = 3 054 Dq(A) = 2 170 Dt = 505 |

-allowed transitions ¹A_{1g} → ¹T_{1g} and ¹A_{1g} → ¹T_{2g}, respectively, in order of increasing energy. The various ligand-field parameters Dq, B and C were evaluated, as given in Table II.

In the electronic spectra of the FBTS complex of rhodium(III), three bands were observed at 21 980 cm⁻¹, 25 970 cm⁻¹ and 33 900 cm⁻¹. The first two weak bands were observed probably due to the splitting of the ¹T_{1g} term (¹E + ¹A) in D_{4h} symmetry¹⁹. The assignments are given in Table 2. The ligand field strength in the xy-plane (Dq E) and the z-plane (Dq A) and the degree of distortion (Dt) were evaluated. The positive value of Dt indicates that the ¹E_g level should lie lower than the ¹A_{2g} level.

The platinum(IV) complexes of SBTS and FBTS were found to be diamagnetic in nature (X_g = -0.427 × 10⁻⁶ c. g. s. and -0.349 × 10⁻⁶ c. g. s. for SBTS and FBTS complexes, respectively) at room temperature. The platinum(IV) is isoelectronic to rhodium(III). The electronic spectra of [Pt(SBTS)₂]Cl₂ exhibit three bands at 24 100 cm⁻¹, 31 250 cm⁻¹ and 37 740 cm⁻¹. These bands suggest the octahedral symmetry for the present complex. The first weak low-energy

TABLE III
 Important IR Bands of the Ligands (SBTS and FBTS) and Their Complexes

| Compound | ν_{OH} cm ⁻¹ | ν_{NH} cm ⁻¹ | Amide I | Amide II | Amide III | ν_{CS} | ν_{CN} | $\nu_{(CO)}$ | $\nu_{(M-O)}$ | $\nu_{(M-N)}$ | $\nu_{(M-S)}$ | $\nu_{(M-Cl)}$ |
|---|--------------------------------|--------------------------------|---------|----------|-----------|-------------------|------------|--------------|---------------|---------------|---------------|----------------|
| SBTS | 3530(s) | 3240 to 3020(s) | 1620(s) | 1570(s) | 1230(m) | 1285(s) 730(s) | 750(s) | — | — | — | — | — |
| FBTS | — | 3140 to 3040(s) | 1615(s) | 1575(s) | 1235(w) | 1280(s) 735(s) | 750(s) | — | — | — | — | — |
| [Ru(SBTS) ₂]Cl | — | 3180 to 3000(s) | 1625(s) | 1560(s) | 1232(m) | 1267(m) 730(m) | 747(s) | 430(m) | 460(m) | 400(m) | — | — |
| [Ru(FBTS) ₂ Cl ₂]Cl | — | 3120 to 3030(s) | 1615(s) | 1552(s) | 1237(w) | 1270(m) 725(m) | 745(m) | — | 452(w) | 405(m) | 346(m) | — |
| [Rh(SBTS) ₂]Cl | — | 3220 to 3060(s) | 1620(s) | 1555(m) | 1237(w) | 1270(s) 720(m) | 742(m) | 437(m) | 457(w) | 395(m) | — | — |
| [Rh(FBTS) ₂ Cl ₂]Cl | — | 3130 to 3015(s) | 1620(s) | 1560(s) | 1232(w) | 1267(m) 728(m) | 745(s) | — | 454(m) | 402(w) | 335(m) | — |
| [Pt(SBTS) ₂]Cl ₂ | — | 3240 to 3020(s) | 1632(s) | 1557(s) | 1228(m) | 1265(m) 720(m) | 755(s) | 432(m) | 452(m) | 415(m) | — | — |
| [Pt(FBTS) ₂ Cl ₂]Cl ₂ | — | 3140 to 3020(s) | 1612(s) | 1547(s) | 1230(w) | 1260(m) 715(m) | 760(s) | — | 450(m) | 425(m) | 342(w) | — |

band can be assigned to the spin-forbidden transition ${}^1A_{1g} \rightarrow {}^3T_{1g}, {}^3T_{2g}$. The other two bands are due to the spin-allowed transitions ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, respectively, in order of increasing energy. The Racah parameters and the ligand-field splitting parameter were evaluated for this complex and are given in Table II.

The electronic spectra of the complex $[Pt(FBTS)_2Cl_2]Cl_2$, exhibit four absorption maxima at $24\,390\text{ cm}^{-1}$, $28\,370\text{ cm}^{-1}$, $32\,790\text{ cm}^{-1}$ and $37\,040\text{ cm}^{-1}$. The first weak low-energy band is assigned to the spin-forbidden transition ${}^1A_{1g} \rightarrow {}^3T_{1g}, {}^3T_{2g}$. The bands observed at $28\,370\text{ cm}^{-1}$ and $32\,790\text{ cm}^{-1}$ were perhaps a consequence of the splitting of the ${}^1T_{1g}$ term (${}^1E_g + {}^1A_{2g}$) due to the lowering of symmetry¹⁹, and were assigned to ${}^1A_{1g} \rightarrow {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1A_{2g}$, respectively. The highest-energy band at $37\,040\text{ cm}^{-1}$ may be assigned to the ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition. The various ligand-field parameters Dq (E), Dq (A) and Dt were evaluated (see Table II).

Study and comparison of the IR spectra of SBTS and its ruthenium, rhodium and platinum metal complexes reveal the disappearance of the bands observed in the free ligand at 3530 cm^{-1} and 1335 cm^{-1} , usually associated with the stretching and deformation of the OH (phenolic) group and thus indicating the loss of the phenolic proton on complexation forming the metal-oxygen link²¹.

The absorption bands in the IR spectra of SBTS, FBTS and their complexes in the region $3240\text{--}3020\text{ cm}^{-1}$ have been assigned to NH vibrations²⁰. The absorption bands around 1620 cm^{-1} , 1570 cm^{-1} , 1230 cm^{-1} and 750 cm^{-1} have been assigned^{22,23} to amide I, amide II plus CN stretch, amide III and SNCO, respectively. There is no appreciable change in the positions and intensities of these bands, thus excluding the possibility of participation of the amido group in chelation. However, a small shift of lowering of the intensity of the bands observed at 1570 cm^{-1} has been observed. The possible reason for this is the participation of the CN group in chelation, whereby the contribution of the CN group to this band is reduced. The changes in the positions and intensities of the free-ligand bands observed at around 1290 cm^{-1} and 730 cm^{-1} on complexation again suggest the participation of the thioketosulphur atom and the unsaturated nitrogen of the CN group in chelation^{1,24}. Several additional bands observed^{21,25} in the low-energy IR spectra of the complexes in the regions $460\text{--}450\text{ cm}^{-1}$, $437\text{--}430\text{ cm}^{-1}$, $425\text{--}400\text{ cm}^{-1}$ and $346\text{--}335\text{ cm}^{-1}$ may perhaps be due to M—N, M—O, M—S and M—Cl vibrations.

EXPERIMENTAL

Chemicals of AnalaR grade were used throughout. The metals used were Johnson-Mathew products. Details of physical measurements, analysis of carbon, hydrogen and nitrogen and synthesis of the ligands (SBTS and FBTS) are the same as described earlier¹⁻³.

Preparation of the Complexes

A general procedure was adopted for the preparation of the complexes of the SBTS and FBTS ligands.

(i) Ruthenium (III) Complexes

A commercial sample of ruthenium(III) chloride (1.0 g) was treated several times with concentrated hydrochloric acid and the solution was evaporated to dryness

to ensure²⁶ complete conversion of ruthenium(IV) into ruthenium(III), which is often present as an impurity in the sample.

The ruthenium chloride thus obtained was dissolved in ethanol (95%) and mixed with 75 ml of an equimolar ligand solution. The optimum pH of the solution (~6.5) was adjusted by the dropwise addition of alcoholic ammonia. This solution was refluxed for one hour and concentrated. The concentrated mass was kept in a refrigerator for two days, where by greyishbrown coloured crystals were obtained. The crystals were separated, washed thoroughly with ethanol and ether, and dried in an oven at 80 °C. Yield ~65%. The loss of water on heating of the complexes at 110 °C corresponds to two molecules of crystallization water.

(ii) Rhodium(III) Complexes

25 ml of an ethanolic solution of rhodium(III) chloride xH_2O (1.0 g) were mixed with 75 ml of an equimolar solution of the ligand. The optimum pH of the mixture was maintained as in procedure (i) and the solution was concentrated to half of its volume. The reddish-brown precipitate was obtained on cooling; it was purified and dried as in procedure (i). Yield ~75%.

(iii) Platinum(IV) Complexes

25 ml of an ethanolic solution of hexachloroplatinic acid (1.0 g) were mixed with 75 ml of an ethanolic solution of the ligand. The optimum pH (~6.5) was adjusted and the solution was concentrated. A pink precipitate was obtained. The precipitate was purified and dried as in procedure (i). Yield ~70%.

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SAŽETAK

Neki kompleksi supstituiranih tiosemikarbazona s platinskim kovinama

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Pripremljeni su kompleksi Ru(III), Rh(III) i Pt(IV) s 1-salicil-4-benzilamidotiosemikarbazonom (SBTS) i 1-(α -)fural-4-benzilamidotiosemikarbazonom (FBTS). Njihova stereokemija predložena je na temelju magnetskih i elektronsko-spektroskopskih ispitivanja. Kompleksi Ru(III) pokazuju i Pt(IV) sa FBTS imaju pseudooktaedarsku simetriju, dok su kompleksi sa SBTS oktaedarski. Izračunani su odgovarajući parametri ligandnog polja. FBTS se veže bidentatno (S,N), a SBTS tridentatno (S,N,O).

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