Platinum Metal Complexes of *N*-Ethylcyclohexyldithiocarbamate

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N-Ethylcyclohexyldithiocarbamate complexes of Pd(II), Pt(II), Ru(III), Rh(III), Ir(III), and Os(IV) have been synthesized and characterized on the basis of electrical conductance, magnetic susceptibility, and spectral (IR, UV, VIS) studies.

The use of fungicides and pesticides with dithiocarbamate ligands has induced a vast amount of biological and biochemical study [1, 2]. The dithiocarbamate moiety is one of those polyatomic groups which can stabilize higher oxidation states of metals [3]. The metal dithiocarbamates throw light on certain interesting structural aspects [4, 5]. Our earlier interest in metal dithiocarbamates [6, 7] continues in the present work wherein a few *N*-ethylcyclohexyldithiocarbamate ($EtcyhxNCS_2$) complexes of platinum metals are synthesized and characterized.

EXPERIMENTAL

$RuCl_3$, $RhCl_3$, $PdCl_2$, $IrCl_3$, $(NH_4)_2OsCl_6$, and K_2PtCl_4 were purchased from Fluka AG, Switzerland. Sodium *N*-ethylcyclohexyldithiocarbamate was prepared by the method of *Gilman* and *Blatt* [8].

An Elico conductivity bridge, model CM-82 was used for conductance measurements. The IR spectra were recorded on a Perkin Elmer grating 621 spectrophotometer, while a Perkin Elmer UV VIS spectrophotometer, model 554 was used for recording electronic spectra. The room temperature magnetic susceptibilities were determined by the Gouy method using $Hg[Co(NCS)_4]$ as the calibrant. The metal ions were estimated by standard methods [9].

Preparation of Complexes

The metal complexes were prepared by adding an aqueous solution of the appropriate metal chloride to an aqueous solution of the ligand in stoichiometric proportions and stirring the mixture for about 15 min at 0—5 °C. In the case of the platinum(II) complex, however, the contents were heated on a water bath for 15 min. The precipitate obtained was washed with cold water and aqueous ethanol and recrystallized from acetone solution. The osmium(IV) complex was obtained by the reaction of $(NH_4)_2OsCl_6$ with the ligand in a 1:5 mole ratio in aqueous methanol for 3 h.

RESULTS AND DISCUSSION

The complexes were found to be soluble in common organic solvents, but insoluble in water. Conductivity measurements revealed that the compounds were nonelectrolytes in nitrobenzene ($\Lambda = 0.25$—$0.30\ \Omega^{-1}\ cm^2\ mol^{-1}$). The analytical data and the physical characteristics are presented in Table 1.

The monodentate or bidentate nature of the dithiocarbamate group is reflected in the ν(C···S) stretching frequency on the infrared spectra. The presence of only one strong band in the $\approx 1000\ cm^{-1}$ region supports the bidentate behaviour of the dithiocarbamates, a doublet being expected in the case of monodentate behaviour [10]. In the present study the ligand showed a doublet at $\tilde{\nu} = 980\ cm^{-1}$ and $1005\ cm^{-1}$, while the complexes exhibited only one strong band in the $(1020 \pm 30)\ cm^{-1}$ region, supporting the chelating nature of the ligand in the complexes. In the case of the Os(IV) complex, besides the sharp singlet at $\tilde{\nu} = 1000\ cm^{-1}$ a doublet appeared at $\tilde{\nu} = 1025\ cm^{-1}$ This indicates that the complex possesses both the chelating and nonchelating dithiocarbamate species.

The absorption band of the thioureide at $\tilde{\nu} \approx 1500\ cm^{-1}$ appearing between that of C—N ($\approx 1300\ cm^{-1}$) and C=N ($\approx 1650\ cm^{-1}$) suggests partial double bond character [3]. In the case of the free ligand the ν(C···N) stretching frequency occurred at $\tilde{\nu} = 1480\ cm^{1}$ Thus, in metal complexes the ν(C···N) vibrational mode appeared at higher frequencies (blue shift) than in the free ligand. This is an indication of the bidentate bonding behaviour of the ligand. When both sulfurs of the dithiocarbamate moiety are coor-

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Table 1. Analytical Data of the M $[EtcyhxNCS_2]_n$ Complexes

M	Colour θ/°C	w_i(found)/% w_i(calc.)/% M	N	S
Ru(III)	Brown	14.91	6.15	28.30
	190—192	14.96	6.17	28.24
Rh(III)	Orange	15.05	6.18	28.23
	208—210	15.11	6.16	28.19
Pd(II)	Orange-yellow	21.44	5.65	25.75
	240	21.49	5.63	25.76
Os(IV)	Green	19.85	5.87	26.80
	165—167	19.89	5.85	26.77
Ir(III)	Orange	24.90	5.47	24.97
	204—206	24.94	5.45	24.93
Pt(II)	Yellow	33.33	4.75	22.00
	231	33.36	4.78	21.80

dinated to the metal ion, the charge density on nitrogen gets substantially reduced. Therefore, it tends to withdraw the charge from the alkyl substituents, thereby increasing the C—N bond order. Hence the dithiocarbamate moiety, acting as a bidentate chelating ligand, exhibits ν(C···N) vibrational frequency higher in position than that of the free ligand. When acting as a monodentate ligand, this stretching frequency is shifted towards a lower wavenumber or remains unchanged at the value of the free ligand [11]. The absorptions at $\tilde{\nu}$ = 375—365 cm^{-1} were assigned to ν(M—S). The relevant IR data are presented in Table 2.

Table 2. IR Spectral Data ($\tilde{\nu}/cm^{-1}$) of the M $[EtcyhxNCS_2]_n$ Complexes

M	ν(C—N)	ν(C—S)	ν(M—S)
Na(I)	1480	980, 1005	
Ru(III)	1500	1020	375
Rh(III)	1505	1010	380
Pd(II)	1495	1015	375
Os(IV)	1480	1000, 1025	365
Ir(III)	1505	1030	370
Pt(II)	1495	1020	365

In the UV region, the complexes showed an intense band at $\lambda_{max} \approx 256$ nm ($\log\{\varepsilon\} \approx 7.0$), arising due to the π—π^* transitions of the N···C···S chromophore [12]. Another band, which was expected to occur at $\lambda_{max} \approx 320$ nm and associated with the inequivalence of the C···S bonds, tended to disappear, showing that the dithiocarbamate ligand was bidentate [13].

Except for the ruthenium(III) complex, the compounds were found to be diamagnetic. The ruthenium(III) complex showed a magnetic moment of 1.82 μ_B, though 2.10 μ_B is expected for the free Ru(III) ion. The discrepancy is due to the low symmetry ligand field [14].

In the visible region the Ru(III) complex showed two spin-forbidden bands at 14000 cm^{-1} ($\log\{\varepsilon\}$ = 1.02) and 17450 cm^{-1} ($\log\{\varepsilon\}$ = 1.90) and one spin-allowed absorption at 22000 cm^{-1} ($\log\{\varepsilon\}$ = 3.51). These may be assigned to $^2T_{2g} \rightarrow {}^4T_{1g}$, $^2T_{2g} \rightarrow {}^4T_{2g}$, and $^2T_{2g} \rightarrow {}^2A_{2g}$, $^2T_{1g}$ transitions, respectively, in agreement with the octahedral environment around the metal ion [15]. For the Rh(III) analog, the bands observed at 22950 cm^{-1} ($\log\{\varepsilon\}$ = 3.05) and 27900 cm^{-1} ($\log\{\varepsilon\}$ = 2.75) are attributed to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively, suggesting an octahedral arrangement [16]. The Pd(II) complex showed absorptions at 1940 cm^{-1} ($\log\{\varepsilon\}$ = 3.46, $^1A_{1g} \rightarrow {}^1A_{2g}$), 23450 cm^{-1} ($\log\{\varepsilon\}$ = 3.38, $^1A_{1g} \rightarrow {}^1B_{1g}$), and 27000 cm^{-1} ($\log\{\varepsilon\}$ = 4.03, $^1A_{1g} \rightarrow {}^1E_g$), suggesting a square-planar geometry [16].

Two intense absorptions observed at 27000 cm^{-1} ($\log\{\varepsilon\}$ = 4.50) and 34100 cm^{-1} ($\log\{\varepsilon\}$ = 5.13) in the case of the Os(IV) complex are of charge transfer origin [17]. These bands are indicative of octahedral symmetry [16]. The Os((IV) complex, therefore, contains two chelating dithiocarbamate groups along the xy-plane and two nonchelating ones along the z-axis. These results are in line with the IR data. The Ir(III) complex exhibited three bands at 26800 cm^{-1} ($\log\{\varepsilon\}$ = 3.83), 29100 cm^{-1} ($\log\{\varepsilon\}$ = 4.16), and 32800 cm^{-1} ($\log\{\varepsilon\}$ = 4.32). While the first two are attributed to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, the third is the charge transfer band [16]. For the Pt(II) complex the absorption bands observed at 16900 cm^{-1} ($\log\{\varepsilon\}$ = 3.08, $^1A_{1g} \rightarrow {}^1A_{2g}$), 20000 cm^{-1} ($\log\{\varepsilon\}$ = 1.65, $^1A_{1g} \rightarrow {}^1B_{1g}$), and 24100 cm^{-1} ($\log\{\varepsilon\}$ = 3.80, $^1A_{1g} \rightarrow {}^1E_g$) are compatible with a square-planar geometry [17]. In the case of the Pd(II) and Pt(II) analogs, the band intensities are higher

than expected. This is attributed to the mixing of ^3E_g or ^1E_g state with all the spin singlets [16].

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