Dithiocarbamate Complexes of Rhodium(III), Iridium(III), Palladium(II) and Platinum(II)

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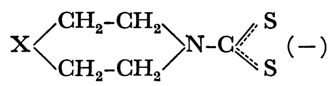
The complexes of rhodium(III), iridium(III), palladium(II) and platinum(II) with piperidine-, piperazine-, *N*-methylpiperazine-, morpholine- and thiomorpholine-dithiocarbamate have been prepared and characterized by spectroscopic methods. From the electronic absorption spectra the values of the ligand field parameters were determined. The nephelauxetic parameters are indicative of a strong covalency in the metal-ligand bond. A monomeric structure for the complexes is suggested. All the new compounds here reported are diamagnetic.

In a previous paper¹⁾ we have discussed the complexes of many transition metals with piperidine-, thiomorpholine- and *N*-methylpiperazine-dithiocarbamate. We report now the preparation and the characterization of new complexes of rhodium(III), iridium(III), palladium(II) and platinum(II) with:



X=CH_2	Pipdtc
X=NH	Pzdtc
X=N-CH_3	CH_3-Pzdtc
X=O	Morphdtc
X=S	Timdtc

in order to investigate particularly the spectrochemical properties of these compounds. This paper is the extension of the previously reported studies on the dithiocarbamates in order to further our present knowledge and to gain new informations concerning the behaviour of the different ligands by substituting the dialkyl derivatives for the heterocyclic dithiocarbamates.

The complexes have been characterized on the basis of vibrational (conventional and far infrared) and electronic spectroscopy and magnetic measurements.

During the first draft on this manuscript Sceney and Magee²⁾ reported the complexes Pd(Pipdtc)$_2$ and pd(Morphdtc)$_2$ that we have included for comparison purposes only.

Results and Discussion

The complexes obtained and some physical properties are reported in Table 1. Solid state electronic spectra are given in Tables 2 and 3. The most important infrared bands are summarized in Table 4.

The metal dithiocarbamates were prepared using the appropriate sodium dithiocarbamate and rhodium trichloride, ammonium esachloroiridate(III), palladium(II) nitrate and potassium tetrachloroplatinate(II) according to the methods described in the experimental section.

The compounds are micro-crystalline, soluble in acetone, *N*,*N*-dimethylformamide and chloroform.

The trisdithiocarbamate derivatives of rhodium(III) and iridium(III) are low-spin type (t^6_{2g}). Solid state electronic spectra confirm an octahedral configuration

Table 1. Analytical data and other physical properties

Compound	Color	Calcd %		Found %		Dec. point
		C	H	C	H	°C
[Rh(Pipdtc)$_3$]	Orange	37.03	5.18	37.31	5.38	298—300
[Rh(Pzdtc)$_3$]	Orange	30.70	4.64	30.76	4.63	293—295
[Rh(CH_3-Pzdtc)$_3$]	Orange	34.38	5.30	34.31	5.36	315—317
[Rh(Morphdtc)$_3$]	Orange	30.55	4.10	30.53	4.07	232—234a)
[Rh(Timdtc)$_3$	Orange	28.24	3.79	28.60	3.64	265—267
[Ir(Pipdtc)$_3$]	Orange-yellow	32.13	4.50	32.06	4.51	318—320
[Ir(Pzdtc)$_3$]	Orange-yellow	26.65	4.03	26.62	3.64	314—316
[Ir(CH_3-Pzdtc)$_3$]	Orange-yellow	30.10	4.63	29.97	4.40	330—332
[Ir(Morphdtc)$_3$]	Orange-yellow	26.53	3.56	26.58	3.65	318—320a)
[Ir(Timdtc)$_3$]	Orange-yellow	24.77	3.33	24.34	3.26	288—290
[Pd(Pzdtc)$_2$]	Yellow	28.00	4.23	28.11	4.23	298—300
[Pd(CH_3-Pzdtc)$_2$]	Yellow	31.53	4.85	31.70	4.44	302—304
[Pd(Timdtc)$_2$]	Yellow	25.94	3.48	26.35	3.34	>350
[Pt(Pipdtc)$_2$]	Bright yellow	27.90	3.90	28.12	3.72	318—320
[Pt(Pzdtc)	Bright yellow	23.20	3.51	22.86	3.21	>350
[Pt(CH_3-Pzdtc)$_2$]	Bright yellow	26.41	4.06	26.72	4.08	>350
[Pt(Morphdtc)$_2$]	Bright yellow	23.12	3.10	23.66	2.89	>350
[Pt(Timdtc)$_2$]	Bright yellow	21.77	2.92	22.10	2.86	>350

a) Melting point.

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Table 2. Electronic spectra (cm^{-1})

Compound	$^1A_{1g}\to{}^1T_{1g}$	$^1A_{1g}\to{}^1T_{2g}$	C. T.	ν_2/ν_1	Δ	B'	β	Z^*
[Rh(Pipdtc)$_3$]	24100	28735		1.19	24840	310	0.43	0.27
[Rh(Pzdtc)$_3$]	23365	28170		1.21	24140	323	0.45	0.31
[Rh(CH$_3$-Pzdtc)$_3$]	24100	29240		1.21	25400	346	0.48	0.38
[Rh(Morphdtc)$_3$]	23420	28820		1.23	24580	366	0.51	0.45
[Rh(Timdtc)$_3$]	23640	29150		1.23	25520	373	0.52	0.47
[Ir(Pipdtc)$_3$]	27250	28820	31750	1.06	28000	100	0.15	
[Ir(Pzdtc)$_3$]	27400	28985	31750	1.06	27640	101	0.15	
[Ir(CH$_3$-Pzdtc)$_3$]	27320	28890	31750	1.06	28000	100	0.15	
[Ir(Morphdtc)$_3$]	27320	28890	—	1.06	28000	100	0.15	
[Ir(Timdtc)$_3$]	27400	29000	30950	1.06	27310	102	0.15	

B is taken to be 720 cm^{-1} for the Rh^{3+} free ion and 660 cm^{-1} for the Ir^{3+} free ion.

Table 3. Electronic spectra (cm^{-1})

Compound	d-d band	C. T.	Δ_1
[Pd(Pipdtc)$_2$]$^{a)}$	22200	—	24300
[Pd(Pzdtc)$_2$]	22330	28010	24430
[Pd(CH$_3$-Pzdtc)$_2$]	22470	27780	24570
[Pd(Morphdtc)$_2$]$^{a)}$	22000	—	24100
[Pd(Timdtc)$_2$]	22730	27550	24830

a) Ref. 2

Table 4. Infrared absorption bands (cm^{-1})

Compound	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	ν(M–S)
PipdtcNa	1465 vs	965 vs	—
PzdtcNa	1460 vs	1000 vs	—
CH$_3$-PzdtcNa	1450 vs	995 s	—
MorphdtcNa	1440 vs	990 s	—
TimdtcNa	1458 vs	995 s	—
[Rh(Pipdtc)$_3$]	1495 vs	985 m	330 m
[Rh(Pzdtc)$_3$	1485 vs	1000 s	330 m
[Rh(CH$_3$-Pzdtc)$_3$]	1490 vs	1000 vs	335 ms
[Rh(Morphdtc)$_3$]	1490 vs	1000 s	330 ms
[Rh(Timdtc)$_3$]	1470 vs	1005 m	335 m
[Ir(Pipdtc)$_3$]	1500 vs	982 ms	323 m
[Ir(Pzdtc)$_3$]	1495 vs	1000 vs	320 m
[Ir(CH-Pzdtc)$_3$]	1495 vs	1000 s	325 m
[Ir(Morphdtc)$_3$]	1495 vs	1000 s	320 m
[Ir(Timdtc)$_3$]	1490 vs	1000 m	320 mw
[Pd(Pipdtc)$_2$]$^{a)}$	1510 vs	972 w	353 m
[Pd(Pzdtc)$_2$]	1500 vs	1010 ms	350 ms
[Pd(CH$_3$-Pzdtc)$_2$]	1505 vs	1000 vs	340 s
[Pd(Morphdtc)$_2$]$^{a)}$	1493 vs	—	346 m
[Pd(Timdtc)$_2$]	1500 vs	1000 m	340 ms
[Pt(Pipdtc)$_2$]	1515 vs	970 m	360 mw, 300 w
[Pt(Pzdtc)$_2$]	1510 vs	1000 vs	350 m, 290 w
[Pt(CH$_3$-Pzdtc)$_2$]	1505 vs	1010 s	380 w, 290 w
[Pt(Morphdtc)$_2$]	1500 vs	1005 s	345 s, 290 ms
[Pt(Timdtc)$_2$]	1510 vs	1005 m	380 vs, 290 mw

a) Ref. 2

of the central atom, Table 2.

The bands positions are similar to those reported with other sulphur coordinating ligands.

The band at somewhat higher energies in the iridum derivatives, *ca.* 31000 cm^{-1}, can be attributed to a charge transfer transition[3,4].

Studies on the electronic spectra of IrS$_6$ complexes are rare, the assignments of the transitions in our complexes were made with the aid of previous reports.[5,6]

The ratios ν_2/ν_1 are in the range 1.19—1.23 and are equal to 1.06 for rhodium and iridium complexes respectively, in very good agreement with the literature data of diethyldithiophosphate derivatives.[7]

The ligand field parameters Δ, B′ and β have been calculated by means of the equations

$$\nu_1 = \Delta - 4B' + 86(B')^2/\Delta \qquad \nu_2 = \Delta + 12B' + 2(B')^2/\Delta$$

and are reported in Table 2. The B' values are of the order of 40—50% of the free ion value in rhodium complexes, and of 15% of the free ion value in iridium derivatives. This fact suggests that there is a considerable orbital overlap with a strong covalency in the metal-ligand σ bond.

The nephelauxetic effect is quite in line with other sulphur-containing chelating agents, which give a very pronounced nephelauxetic decrease of β[6]. It is well known that decreasing values of β are associated with a reduction in the effective positive charge of the metal ion and with an increasing tendency to be reduced to the next lower oxidation state. For the second-row transition metals the variation of the Racah interelectronic repulsion parameter with cation charge Z*, and the number q of electrons in the partly filled d shell, is well-expressed by the relation:

$$B'(\mathrm{cm}^{-1}) = 472 + 28q + 50(Z^*+1) - 500/(Z^*+1)$$

The effective ionic charges of the rhodium complexes have been found (Table 2) to lie in the range 0.27—0.47, considerably below the formal +3 oxidation state of rhodium. Rhodium(III) complexes with oxygen donors have effective charges[8] in the range 1.65—2.03.

In the electronic spectra of palladium(II) derivatives, recorded in solid state as nujol mulls, only the first band, mostly a shoulder, at 22300—22700 cm^{-1}, can be considered a d-d transition. The great intensity of the second band suggests that it may be charge-transfer in character rather than ligand-field. The d-d band can be assigned to the $^1A_g\to{}^1B_{1g}$ ($x^2-y^2\to xy$) transition.[9] By assuming a value of $F_2=10F_4=$ 600 cm^{-1} for the Slater-Condon interelectronic repulsion parameters,[10] it is possible to derive from the first spin-allowed d-d transition the value of Δ_1 being

$\nu_1+3.5F_2=\Delta_1$ (Table 3). The fact that the first d-d band is at higher energy for palladium(II) (22300—22700 $\mathrm{cm^{-1}}$) than for nickel(II) (16000—16100 $\mathrm{cm^{-1}}$)[1] agrees with the spectrochemical order of these metal ions.

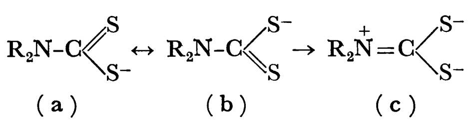
Infrared spectral studies of dithiocarbamates have not been carried out in detail, it is quite difficult to assign the bands being most of them very highly coupled. A normal coordinate analysis has been carried out by Nakamoto[11] for the complex $[\mathrm{Pt(S_2CNH_2)_2}]$ and by Dugarprased[12] for the derivative $[\mathrm{Ni(Me_2dtc)_2}]$.

The ν(C=N) and ν(C=S) stretching frequencies for the free ligand sodium salts and for our complexes are reported in Table 4. The medium band present in all the studied complexes in the range 835—790 $\mathrm{cm^{-1}}$ is assigned to a C–S stretching coupled with the $\mathrm{NH_2}$ rocking mode.

Very little differences have been observed in the infrared spectra of the complexes on changing the heterocyclic ring in the system.

The ν(C=N) stretching mode of the dithiocarbamate used as ligands in this work is at lower wave numbers than ν(C=N) of diethyldithiocarbamate, 1477 $\mathrm{cm^{-1}}$. This difference is reflected in the complexes too, in fact if we compare the dithiocarbamates of iridium, palladium and platinum we observe that ν(C=N) follows the order: $\mathrm{Me_2dtc}>\mathrm{Et_2dtc}>\mathrm{Pipdtc}>n\mathrm{Pr_2dtc}>n\mathrm{Bu_2dtc}>\mathrm{CH_3\text{-}Pzdtc}>\mathrm{Pzdtc}>\mathrm{Morphdtc}>\mathrm{Timdtc}>i\mathrm{Pr_2dtc}>i\mathrm{Bu_2dtc}>\mathrm{CycHex_2dtc}$.

The structure of the dithiocomplexes can be represented by the following formalism:



The extent to which resonance form (c) contributes to the structure and its effects on the physical and chemical properties of the complexes has been extensively studied. Chatt and co-workers[13] concluded that resonance form (c) does indeed contribute to the structure to a considerable extent.

From the above reported sequence of ν(C=N) we could conclude that the contribution of structure (c) is greatest for the corresponding dialkyl complexes, lower for more complex aliphatic chain and it is relatively small for heterocyclic derivatives. Perhaps because of the rigid heterocyclic ring system which shows less tendency to release electrons to the nitrogen-carbon bond and, as consequence, this bond has a less double-bond character.

In the far infrared region the bands of the ligands appear unchanged in the complexes spectra. New bands appear in the rhodium derivatives at *ca.* 330 $\mathrm{cm^{-1}}$ and at *ca.* 325 $\mathrm{cm^{-1}}$ in iridium complexes (Table 4). These absorption bands, absent in the spectra of the free ligand and in the spectra of palladium and platinum derivatives, are to be due to a metal ligand interaction. We could tentatively assign these values to a ν(Rh-S) and ν(Ir-S) stretching vibrations respectively.

According to Sceney[2] and Nakamoto[11] we can assign the palladium-sulphur and platinum-sulphur vibration modes in the ranges 353—340 $\mathrm{cm^{-1}}$ and 380—345 $\mathrm{cm^{-1}}$, 300—290 $\mathrm{cm^{-1}}$ respectively, the bands at 300—290 $\mathrm{cm^{-1}}$ in platinum complexes being coupled with a ring deformation mode.

Experimental

Preparation of the Ligands. The sodium salt of the piperidine-, thiomorpholine- and *N*-methylpiperazinedithiocarbamate have been prepared as previously described.[1] The sodium morpholinedithiocarbamate has been prepared by treating morpholine in dry ethyl ether with carbon disulphide and adding under vigorous stirring sodium hydroxide during four hr. Molar ratios amine : $\mathrm{CS_2}$: NaOH= 1 : 1 : 1. The crude product was recrystallized from isopropyl alcohol. The sodium piperazinedithiocarbamate has been prepared by the same method, starting with piperazine dissolved in dry ethyl ether and isopropyl alcohol. The crude product was recrystallized from methanol/ethyl ether.

Preparation of the Complexes. The complexes have been obtained by adding an aqueous solution of rhodium trichloride, ammonium esachloroiridate(III), palladium nitrate, potassium tetrachloroplatinate(II) to the dithiocarbamate dissolved in methanol or water, at room temperature. The precipitate was filtered, washed with methanol and dried over $\mathrm{P_4O_{10}}$.

Infrared Spectra. The IR spectra have been recorded in the range 4000—200 $\mathrm{cm^{-1}}$ with Perkin-Elmer 457 and 225 spectrophotometers as KBr discs and nujol mulls between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing dry nitrogen.

Visible and UV Spectra. Solid state electronic spectra have been recorded with a Shimadzu MPS-50L spectrophotometer.

Magnetic Susceptibility Measurements. These were carried out by Gouy's method. Molecular susceptibilities were corrected for diamagnetism of the component atoms by use of the Pascal's constants. All the complexes resulted diamagnetic.

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