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Diselenocarbamates with Square-Planar Stereochemistry

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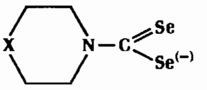
Nickel(II), palladium(II), platinum(II) and copper(II) complexes were prepared with piperidine-, morpholine- and thiomorpholine-diselenocarbamates (pidsc, modsc and tmdsc) as chelating ligands. Their electronic spectra were investigated and interpreted to obtain the dsc position in the spectrochemical series for square-planar derivatives. From the i.r. spectra the M–Se vibrations were identified and an empirical trend for this bond strength is proposed. The N–C bond strongly increases its double-bond character on passing from the ligands to the complexes.

Introduction

In the last few years many workers have studied the behaviour of N,N-dialkyldithiocarbamates and their transition or non-transition metal complexes, while as far as the diselenocarbamates are concerned the data available are still very limited[1–4].

In a previous paper[5] we reported on a kinetic study of the N–C bond cleavage in acidic media for the homogeneous series of ions:



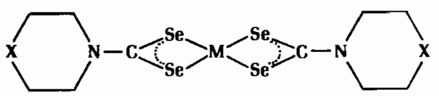
where X =		
	CH_2	*pidsc*
	O	*modsc*
	S	*tmdsc*
	HN	*pzdsc*
	CH_3N	Me-*pzdsc*

Comparing these results with those given previously for the corresponding carbamates and dithiocarbamates[6–7] we observe that the N–C linkage exhibits a stronger double-bond character in the diseleno-series and this fact may be responsible for the increased kinetic stability.

In the present paper we characterize the square-planar complexes of nickel(II), palladium(II), platinum(II) and copper(II) with *pidsc, modsc* and *tmdsc* as chelating ligands. In a later work we expect to use these materials in a kinetic study in order to point out the influence of the coordination to the metal on the N–C bond cleavage reaction.

Results and Discussion

All compounds, prepared by double exchange reaction (see Experimental), are non electrolytes as they have a general formula ML_2:



The analytical data and some physical properties are reported in Table I.

Magnetic measurements demonstrate that nickel(II), palladium(II) and platinum(II) derivatives are, as usual, diamagnetic while the copper(II) complexes are paramagnetic showing, at room temperature, values typical of one unpaired spin (1.72–1.75 B.M.).

The electronic spectra of the free ligands inner salts (*i.e. piHpidsc, moHmodsc, tmHtmdsc*) show two strong absorptions attributed to $\pi \to \pi^*$ and $n \to \pi^*$ transitions[8–13] (Table II).

In the electronic spectra of nickel(II) derivatives five maxima are present in the range 40.000–5.000 cm^{-1} while in the palladium(II) and platinum(II) ones only four appear.

The shoulder sometimes appearing near 35 kK can be attributed to the $L(\pi) \to L(\pi^*)$ internal transition of the ligand, slightly shifted towards higher energies in nickel(II) or towards lower energies in palladium(II) derivatives as a consequence of coordinated bond formation.

The two series of maxima at high energies show ε values ranging between 76,000 and 18,000 mol^{-1} cm^2. Consequently these maxima are charge-transfer absorptions which, coherently with previously reported spectral data for square-planar metal complexes[14–16], could be labelled as $L(\sigma) \to M$ and $L(\pi) \to M$ transitions. On going from nickel to platinum derivatives the $L(\sigma) \to M$ and $L(\pi) \to M$ wavenumbers show two opposite trends, $Ni > Pd > Pt$ and $Ni < Pd < Pt$, respectively.

On the basis of ε values the maxima in the range 23.0–26.7 kK could be attributed to $M \to L$ charge transfer, the energy trend being $Ni < Pd < Pt$. For nickel only an additional maximum is present near

TABLE I. Analytical Data and Some Physical Properties.

Compounds	Colour	Dec. p. °C	Calcd % M	Calcd % C	Calcd % H	Found % M	Found % C	Found % H	B.M.	Solubility
Ni(*pidsc*)$_2$	Pale Green	220	10.4	25.4	3.6	10.4	25.8	3.7	diam	a
Ni(*modsc*)$_2$	Pale Green	210	10.3	21.0	2.9	10.1	21.1	3.1	diam	a
Ni(*tmdsc*)$_2$	Pale Green	195	9.7	19.9	2.7	9.9	20.9	2.8	diam	a
Pd(*pidsc*)$_2$	Yellow	230	17.3	23.6	3.3	–	23.5	3.5	diam	b
Pd(*modsc*)$_2$	Yellow	215	17.2	19.4	2.6	–	19.5	3.0	diam	b
Pd(*tmdsc*)$_2$	Pale Orange	200	16.3	18.5	2.5	–	18.8	2.6	diam	b
Pt(*pidsc*)$_2$	Yellow	215	27.7	20.5	2.9	–	20.9	3.1	diam	b
Pt(*modsc*)$_2$	Yellow	210	27.6	17.0	2.3	–	16.9	2.2	diam	b
Pt(*tmdsc*)$_2$	Pale Orange	200	26.4	16.2	2.2	–	16.5	2.2	diam	b
Cu(*pidsc*)$_2$	Brown	235	11.1	25.2	3.5	11.3	24.6	3.4	1.75	a
Cu(*modsc*)$_2$	Brown	220	11.0	20.9	2.8	11.0	20.5	2.9	1.75	a
Cu(*tmdsc*)$_2$	Brown	215	10.4	19.8	2.7	10.1	20.2	2.8	1.72	a

[a] Soluble in acetone, dichloromethane, nitrobenzene; insoluble in water, ethanol, diethylether. [b] Slightly soluble in acetone, dichloromethane, nitrobenzene; insoluble in the other common solvents. All compounds are non-electrolytes.

TABLE II. Electronic Spectral Data (wavenumbers in kK; logε in parenthesis).[a]

	L(σ)$\to$M	L(π)$\to$L(π^*)	L(π)$\to$M	M$\to$L(π)		*d–d*
Ni(*pidsc*)$_2$	38.9(4.60)		27.8(4.53)	23.2(3.89)	19.0(2.70)	14.8(2.22)
Ni(*modsc*)$_2$	38.3(4.47)	36.8sh	27.8(4.53)	23.0(3.53)	20.7(3.16)	14.5(2.23)
Ni(*tmdsc*)$_2$	38.5(4.51)	36.4sh	27.8(4.59)	23.0(3.80)	20.8(3.30)	14.1(2.18)
Pd(*pidsc*)$_2$	38.0(4.28)	34.0sh	30.6(4.81)	26.0sh		20.7(2.58)
Pd(*modsc*)$_2$	37.8(4.30)	34.0sh	30.3(4.88)	25.5(3.85)		20.4(2.60)
Pd(*tmdsc*)$_2$	37.9(4.26)	33.6sh	30.4(4.57)	25.5(3.60)		19.6(2.83)
Pt(*pidsc*)$_2$	35.2(4.60)		32.0sh	26.7(4.30)		23.5(3.44)
Pt(*modsc*)$_2$	35.2(4.65)		31.8sh	26.4(4.34)		23.1(3.43)
Pt(*tmdsc*)$_2$	35.2(4.63)		31.6sh	26.5(4.28)		22.6(3.37)
Cu(*pidsc*)$_2$		34.2(4.57)	30.8(4.41)	20.1(4.10)		16.5(3.52)
Cu(*modsc*)$_2$		33.8(4.16)	30.5(3.86)	20.1(3.60)		16.5sh
Cu(*tmdsc*)$_2$		33.8(4.50)	30.5(4.16)	20.0(4.07)		16.5sh

[a] All spectra were recorded in dichloromethane solutions. For the free ligands: $\pi\to\pi^*$ 35.3(*pidsc*), 34.5(*modsc*), 35.5(*tmdsc*); n$\to\pi^*$ 31.2, 31.2, 31.9 kK, respectively.

20 kK whose ε value of $\sim 10^3$ suggests a charge transfer character rather than a *d–d* transition.

Only one *d–d* band is observed for nickel complexes near 14.5 kK with ε values of about 150. This maximum is shifted to higher energies in the electronic spectra of palladium(II) and platinum(II) derivatives, in agreement with the spectrochemical order of these metals, and its intensity is increased. Since for the platinum derivatives the values range between 2,300 and 2,800, in order to obtain a confirmation of the transition *d–d* character, we used the equation:

$$\bar{\nu}(L\to L^*) = \bar{\nu}(L\to M) + \bar{\nu}(M\to L) - \bar{\nu}(d\text{–}d) + \text{e.r.}$$

proposed by Latham and coworkers[15], where the wavenumber of internal ligand transition is related to those of the lowest L→M and M→L ones; furthermore the e.r. term "is the difference in inter-electronic repulsion energies of the four excited states involved". This term, which is constant in a series of electronically similar complexes, was evaluated by us at about 1.6 kK, using the assignments for nickel derivatives reported above. The resulting estimated *d–d* wavenumbers for palladium and platinum complexes are reported in Table III and are in good agreement with the experimental results.

Assuming values of 800 cm^{-1} for nickel and 600 cm^{-1} for palladium and platinum for the Slater–Condon F$_2$ parameter the Δ_1 value can be derived from the equation $\Delta_1 = \bar{\nu}_1 + 3.5\ F_2$. In Table IV our Δ_1 values are compared with those available in literature for many ligands and the following spectrochemical series for square-planar complexes of Ni(II), Pd(II) and Pt(II)

TABLE III. Evaluation of *d–d* Wavenumbers (kK) for Pd(II) and Pt(II) Complexes by Latham's Equation (ref. 15).

Complexes	Calcd	Found
Pd(*pidsc*)$_2$	20.2	20.7
Pd(*modsc*)$_2$	19.6	20.4
Pd(*tmdsc*)$_2$	19.6	19.6
Pt(*pidsc*)$_2$	25.1	23.5
Pt(*modsc*)$_2$	24.6	23.1
Pt(*tmdsc*)$_2$	24.5	23.1

TABLE IV. Orbital Parameter (Δ_1) Values (kK) for Some Square-planar Complexes of Ni(II), Pd(II) and Pt(II).

Ligand[a]	Ref.	Ni	Pd	Pt
pidsc	–	17.6	22.8	25.6
modsc	–	17.3	22.5	28.2
tmdsc	–	16.9	21.7	24.7
pidtc	17	16.0	24.3	–
modtc	17	16.0	24.1	–
tmdtc	17	16.0	24.8	–
Et$_2$dtc	18	18.8	–	–
Et$_2$dsc	2	17.6	22.7	–
mnt	14	14.5	17.8	20.6
dtp	19	17.3	23.9	25.9
CN	20	25.3	>30	>30
Br	20	–	18.1	21.8
Cl	20	–	18.8	23.1
dto	15	20.5	28.1	32.1
xan	21	18.3	–	–
dφg	18	25.0	–	–
dmp	22	19.0	–	–

[a] *mnt* = $S_2C_2(CN)_2^{2-}$; *dtp* = $S_2P(OC_2H_5)_2^-$; *xan* = $C_2H_5OCS_2^-$; *dφg* = diphenylglyoximate; *Et$_2$dtc* = diethyldithiocarbamate$^-$; *Et$_2$dsc* = diethyldiselenocarbamate$^-$; *dto* = dithioxalate^{2-}.

is obtained: mnt < Br < Cl < dtp ≅ dtc ≈ dsc < xan < dmp < dφg < CN.

Therefore the spectrochemical resemblance between dithio- and diseleno-carbamates is very striking.

As far as the copper(II) derivatives are concerned, we observe that these compounds may be square-planar in solution, like some complexes previously described[23–25] with chelating sulphurated ligands, although for *dtc* ones a penta-coordinate environment is shown for the metal atom by X-ray analysis[26–28]. In all cases the absorption at 16.5 kK could be due to the *d–d* transition ($d_{x^2-y^2} \rightarrow d_{xy}$) coherently with the value of 16.0 kK obtained for copper diethyldithiocarbamate[29] and of 15.1 kK for Cu(i-*mnt*)$_2^{2-}$ [30].

The most important infrared absorptions of the free ligands are those lying in the ranges 1,500–1,400, 860–830 and 520–360 cm^{-1} (Table V).

In the first range two very strong bands, due to the prevailing contribution of ν(CN) and δ(CH$_2$) modes[31–36], are always present. By contrast, the bands occurring at 854 ± 3, 832 ± 2, 512 ± 7 and 370 ± 6 cm^{-1} are strongly affected by selenation, as clearly evidenced by comparison with the corresponding absorptions of the dithiocarbamates *pidtc*, *modtc* and *tmdtc* (983 ± 8, 867 ± 15, 585 ± 30, 485 ± 5 cm^{-1}). This fact postulates that the prevailing contribution to these vibrations is connected with the CSe$_2$ group.

TABLE V. The Most Important Infrared Absorptions.

Compounds[a]	Approximate Description									
	ν(CN)+δ(CH$_2$)			ν(CNC)+ν(CSe$_2$)		ν(CSe$_2$)				ν(M–Se)
	cm^{-1}	Δ	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	Δ	cm^{-1}	Δ	cm^{-1}
pidsc	1473s	–	1425s	851m	830s	510m	–	370m	–	–
Ni(*pidsc*)$_2$	1505vs	+32	1432vs	850sh	841s	471w	–39	325s	–45	266w
Pd(*pidsc*)$_2$	1500vs	+27	1432vs	852s	840s	476m	–34	320mw	–50	259m
Pt(*pidsc*)$_2$	1510vs	+37	1436vs	854m	841s	470m	–40	309m	–61	242ms
Cu(*pidsc*)$_2$	1495s	+22	1438vs	841s	830m	470m	–40	304m	–65	261s
modsc	1445s	–	1415s	854m	835s	519m	–	366m	–	–
Ni(*modsc*)$_2$	1515–1498vs	+70	1428vs	865s	845m	485m	–34	322ms	–44	284–277w
Pd(*modsc*)$_2$	1495vs	+50	1420vs	867s	829m	487s	–32	324m	–42	259s
Pt(*modsc*)$_2$	1515vs	+70	1422vs	869s	836m	485s	–34	325w	–41	239ms
Cu(*modsc*)$_2$	1480vs	+35	1422vs	869s	851m	482s	–37	311s	–55	266s
tmdsc	1467vs	–	1413s	856s	–	507m	–	375w	–	–
Ni(*tmdsc*)$_2$	1495vs	+28	1428s	870s	830w	450w	–57	320w	–55	285w
Pd(*tmdsc*)$_2$	1485vs	+18	1425vs	865m	830w			309vw	–66	263m
Pt(*tmdsc*)$_2$	1508vs	+41	1431vs	868s	830vw	430w?				239m
Cu(*tmdsc*)$_2$	1470vs	+3	1425vs	868s	830w	416w?				234m

[a] The free ligand spectra were recorded as potassium salts.

On going from the ligands to the complexes, we observe: (i) The two first-range absorptions move towards higher wavenumbers and, sometimes, they are split into four maxima. The shift trend is Pt>Ni>Pd >Cu and is more marked in *modsc* derivatives; (ii) The bands near 850 and 830 cm^{-1} are slightly affected by coordination, moving towards higher energies by about 10 cm^{-1} and changing their intensities ratio; (iii) By contrast, the two bands near 512 and 370 cm^{-1} move towards lower energies and, generally, decrease in intensity; (iv) In all spectra a new medium–strong band appears in the range 285–235 cm^{-1}.

Since the absorptions most affected by selenation and, in particular, those near 500 and 370 cm^{-1}, are strongly affected by the consequences of coordinated bond formation, we believe that the chromophore group is of the MSe_4-type. Starting from this assumption, the new band near 250 cm^{-1} (whose wavenumber value decreases in the order nickel, copper, palladium, platinum) can be attributed to the stretching of the M–Se bond. This assignment is also supported by the facts that the ν(M–S) absorption has been found in the range 390–350 cm^{-1} for the corresponding dithiocarbamates of the same amines[17,37] and that a negative shift of about 100 cm^{-1} is the expected value on passing from sulphur to selenium derivatives.

Taking into account the relative reduced mass values of the four metals, the M–Se bond strength appears to decrease in the order Pt>Pd>Ni>Cu.

As far as the ν(CN) is concerned, the relevant positive shift points to an increase of the N–C double bond character on going from the free ligands to the complexes. It is known[4] that this shift is stronger for a square-planar stereochemistry than for tetrahedral or octahedral ones. Because the shift values for the copper derivatives are the lowest in the series, these compounds may have a distorted square-planar geometry in the solid state as a consequence of possible intermolecular interactions.

Experimental

Preparation of the Ligands and Complexes

The carbon diselenide prepared by the reaction

$$CH_2Cl_2 + Se \xrightarrow{N_2,\ 560^\circ C} CSe_2 + 2HCl$$

and purified by distillation (46°C; 50 mm Hg) was added dropwise under nitrogen and vigorous stirring to a slight excess of amine in diethylether obtaining the inner salt *AmHAmdsc*. The crude product was recrystallised from a methylene chloride/ligroin mixture. The *piHpidsc, moHmodsc, tmHtmdsc* salts are crystalline, yellow in colour, soluble in water, acetone, ethyl alcohol or methylene chloride. All complexes were obtained at room temperature by a double exchange reaction carried out in aqueous solution with the stoichiometric amount of the diselenocarbamate inner salt and the required metal chloride. The products were purified by recrystallization or TLC. Analytical data and some physical properties are reported in Table I.

UV–Visible Spectrophotometric Measurements

The electronic spectra were recorded with a Pye Unicam SP 700 C spectrophotometer in CH_2Cl_2 solution working in the range 40,000–5,000 cm^{-1}.

Infrared Spectra

The IR spectra were recorded in the range 4,000 to 200 cm^{-1} with a Perkin–Elmer 325 instrument as KBr discs or as nujol mulls between CsI plates.

Other Measurements

Conductivity measurements carried out in nitrobenzene by a WTW-LBR type bridge showed that all compounds are non-electrolytes; magnetic measurements, carried out at room temperature by Gouy's method and with a Newport Instrument, showed that platinum(II), palladium(II) and nickel(II) derivatives are diamagnetic while the copper(II) ones are paramagnetic with μ = 1.73–1.75 B.M.

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