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Diselenocarbamates with Tetrahedral, Octahedral or Square-Pyramidal Stereochemistry

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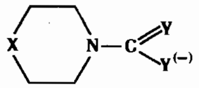
Tetrahedral of Group II B metals and octahedral diselenocarbamates of iron(III), cobalt(III) and chromium(III) were isolated as well as some square-pyramidal Fe(dsc)$_2$X (where X = Cl, Br, I) derivatives. The magnetic moment values, infrared and electronic spectra are reported and interpreted to obtain the ligand field parameters and the selenium nephelauxetic effect. The increase of the N–C double bond character with coordination is pointed out and discussed in comparison with the corresponding dtc derivatives.

Introduction

In previous papers[1–3] we reported on a kinetic study of the N–C bond cleavage in acidic aqueous media for the homogeneous series of ions:



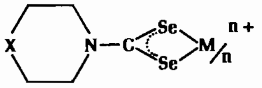
where X =	CH_2	and	Y =	O
	O			S
	S			Se
	HN			
	CH_3N			

Comparing the results obtained for the diselenocarbamate series with those for the corresponding carbamates and dithiocarbamates we point out that the greater kinetic stability of diseleno derivatives could be correlated with the stronger double bond character of the N–C linkage. In order to better investigate this we have prepared and characterized some square-planar complexes of nickel(II), palladium(II), platinum(II) and copper(II) with piperidine-, morpholine- and thiomorpholine-diselenocarbamates (*pidsc, modsc* and *tmdsc*, respectively) as chelating ligands[4]. In fact on going from the free ligands to the complexes the double bond character of the N–C linkage strongly increases. Now a kinetic study of the N–C bond cleavage is in progress with these complexes as substrates.

In the present paper we describe the preparation and characterization of the complexes of zinc(II), cadmium(II), mercury(II), chromium(III), iron(III), cobalt(II) and (III) with the same ligands.

Results and Discussion

The diselenocarbamates react with the metal chlorides by a double exchange to give non-electrolyte complexes having a four membered chelate ring:



where X =	CH_2	M(*pidsc*)$_n$
	O	M(*modsc*)$_n$
	S	M(*tmdsc*)$_n$

Only iron(III) gives a pentacoordinate polyhedron as well, completed by an apical chlorine atom, Fe (*ligand*)$_2$Cl. The analytical data are listed in Table I while the detailed conditions of the reactions are reported in the Experimental.

Group II B Derivatives

The colour of the complexes changes from white to yellow on going from the zinc to the mercury derivatives. All compounds are diamagnetic and have the general formula M(*ligand*)$_2$ except compound IX for which the analytical data are consistent with the formulation Hg(*tmdsc*)Cl. The electronic spectra of a d^{10} system show, of course, the characteristic internal ligand absorptions which fall near 35.0 and 31.0 kK and were previously assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions[5–10].

As reported earlier[4] the two infrared absorptions of the free ligands near 1450 cm^{-1} are prevailingly due to $\nu(CN) + \delta(CH_2)$ modes while those in the range 860–830, near 510 and 360 cm^{-1}, being strongly affected by selenation, are associated with the CSe_2 group vibrations. In Table II the most important absorption

TABLE I. Analytical Data and Some Physical Properties.

	Compounds	Colour	Dec. p. °C	Calcd %		Found %		B.M.	Solubility
				C	H	C	H		
I	Zn(*pidsc*)$_2$	White	268	25.1	3.5	25.3	3.7	Diam.	a
II	Zn(*modsc*)$_2$	White	261	20.8	2.8	21.1	2.9	Diam.	a
III	Zn(*tmdsc*)$_2$	White	255	19.7	2.6	20.4	2.7	Diam.	a
IV	Cd(*pidsc*)$_2$	Pale Yellow	265	23.3	3.3	23.8	3.4	Diam.	a
V	Cd(*modsc*)$_2$	Pale Yellow	249	19.2	2.6	19.3	2.9	Diam.	a
VI	Cd(*tmdsc*)$_2$	Pale Yellow	245	18.3	2.5	18.8	2.6	Diam.	a
VII	Hg(*pidsc*)$_2$	Yellow	244	20.3	2.9	20.3	2.9	Diam.	a
VIII	Hg(*modsc*)$_2$	Yellow	239	16.9	2.3	17.1	2.4	Diam.	a
IX	Hg(*tmdsc*)Cl*	Yellow	170	11.8	1.6	11.4	1.6	Diam.	b
X	Fe(*pidsc*)$_2$Cl	Violet	210**	24.0	3.4	23.7	3.4	3.87	c
XI	Fe(*modsc*)$_2$Cl	Violet	–	19.9	2.7	20.7	3.2	–	c
XII	Fe(*pidsc*)$_3$	Brown	–	26.4	3.7	26.8	3.6	2.25	c
XIII	Fe(*modsc*)$_3$	Brown	235	21.9	2.9	21.7	2.8	1.99	c
XIV	Fe(*tmdsc*)$_3$	Brown	–	20.7	2.8	20.9	3.1	3.46	c
XV	Co(*pidsc*)$_3$	Brown	205	26.4	3.7	26.8	4.3	Diam.	c
XVI	Co(*modsc*)$_3$	Brown	185	21.8	2.6	21.9	3.1	Diam.	c
XVII	Co(*tmdsc*)$_3$	Brown	185	20.6	2.7	20.3	2.9	Diam.	c
XVIII	Cr(*pidsc*)$_3$	Deep Green	295	26.6	3.7	26.8	3.8	3.85	a
XIX	Cr(*modsc*)$_3$	Deep Green	285	22.0	3.0	21.8	3.1	3.87	a
XX	Cr(*tmdsc*)$_3$	Deep Green	–	20.7	2.8	20.5	2.9	3.86	a

* Compound IX, Hg% calcd 39.5, found 40.8. ** Melting point.

[a] Soluble in acetone, dichloromethane, nitrobenzene; insoluble in water, ethanol, diethylether. [b] Insoluble in the same solvents. [c] Very soluble in the same solvents.

TABLE II. The Most Important Infrared Absorptions in the Tetrahedral Complexes.

		Approximate Description									
		ν(CN)+δ(CH$_2$)			ν(CNC)+ν(CSe$_2$)		ν(CSe$_2$)				ν(MSe)
	Compounds	cm^{-1}	Δ	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	Δ	cm^{-1}	Δ	cm^{-1}
	pidsc	1473m	–	1425s	851m	830s	510m	–	372m	–	–
I	Zn(*pidsc*)$_2$	1480vs	+7	1435s	851s	840s	472m	–38	355m	–17	263s
IV	Cd(*pidsc*)$_2$	1482vs	+9	1430s	851m	835s	470ms	–40	363w	–9	270s
VII	Hg(*pidsc*)$_2$	1490vs	+17	1432vs	851m	830s	469ms	–41	365s	–7	264s
	modsc	1445s	–	1415s	854m	835s	519m	–	366m	–	–
II	Zn(*modsc*)$_2$	1490vs	+45	1427s	865s	845m	480ms	–39	360m	–6	273s 257s
V	Cd(*modsc*)$_2$	1472vs[a]	+27	1422s[a]	871s	846ms	482ms	–37	353s	–13	268vs
VIII	Hg(*modsc*)$_2$	1458vs[a]	+13	1416s[a]	868vs	841m	478ms	–41	308m	–58	259m
	tmdsc	1467s	–	1413s	856s		507m	–	389m	–	–
III	Zn(*tmdsc*)$_2$	1478s	+11	1421s	862s	834w	466vw	–41	380w	–9	260s 215s
VI	Cd(*tmdsc*)$_2$				860s	833w	505w	–2	380w	–9	238m 209m
IX	Hg(*tmdsc*)Cl	1490s	+23	1425s	850s						

[a] Split in two bands. The free ligand spectra were recorded as potassium salts.

wavenumbers of the complexes are compared with the free ligand values. As can be seen clearly, the band near 1450 cm^{-1} is strongly shifted towards higher energies as a consequence of an increase of the double bond character of the N–C linkage on coordination; this positive shift is more marked in the *modsc* derivatives than in those of the other two ligands. The two absorptions near 850 cm^{-1} are slightly affected by coordination whereas those at 510 and 370 cm^{-1} move towards lower energies as a consequence of the interaction between selenium and metal atoms. Furthermore in the range 270–240 cm^{-1} one or sometimes two new strong bands appear which are probably due to the ν(M–Se) modes, which could be the ν_3 and

ν_4 for a tetrahedral environment. However it is noteworthy that in the zinc diethyldithiocarbamate the metal atom is coordinated with five sulphur atoms in a distorted bipyramidal structure[11].

As far as the compound Hg(*tmdsc*)Cl (IX) is concerned, it could be interpreted in three different ways: (i) The metal atom is *sp* bi-coordinate with a chlorine atom and one of the two selenium atoms of the ligand; (ii) The complex is tetrahedral and dimeric with the chlorine atom bridged; (iii) The coordination polyhedron is tetrahedral and formed by the two selenium atoms of the diselenocarbamate group, the chlorine and the sulphur atom (X substituent of the *tmdsc* ligand) in a polymeric structure. The hypothesis (iii) is strongly supported by the following evidence: (a) compound IX is completely insoluble in the most common solvents; (b) mercury forms this compound with *tmdsc* only, which is the only ligand with sulphur as an X substituent. In the (iii) hypothesis the *tmdsc* acts as a tridentate bridging ligand.

Iron Derivatives

By reaction of Fe_2Cl_6 with the appropriate ligand a mixture of Fe(*dsc*)$_3$ (brown) and Fe(*dsc*)$_2$Cl (violet) is always obtained together with traces of an unidentified golden yellow product. In the *pidsc* case the pentacoordinate species is predominant but with *modsc* and *tmdsc* this compound appears in traces only. The two compounds are separable by fractional precipitation from dichloromethane/cyclohexane. In every case the pentacoordinate derivatives are easily obtained by shaking the pure Fe(*dsc*)$_3$ solution with the appropriate aqueous hydrohalic acid:

$$\mathrm{Fe}(dsc)_3 + \mathrm{HX} \rightarrow \mathrm{Fe}(dsc)_2\mathrm{X} + dsc\mathrm{H}$$

The X-ray crystal analysis of monochlorobis(N,N-diethyldithiocarbamate)iron(III) confirmed the monomeric square-pyramidal structure of this type of compounds[12].

In our pentacoordinate diselenocarbamate derivatives the magnetic moment corresponds to three unpaired electrons (S = 3/2), as in the dithiocarbamates, while the stretching Fe–Cl at 311 cm^{-1} confirms the presence of chlorine atom in the coordination sphere. On the other hand, on going from chlorine to iodine derivatives a red shift is also observed in the electronic spectra (Table III). These spectra are particularly rich in absorptions, some of which being due to ligand → ligand or ligand–metal charge transfers. The absorptions near 8.5 and 6.1 kK, whose ε values are of few units, are certainly *d–d* transitions, and the same nature may also be tentatively attributed to the 14.6 kK absorption.

In the infrared region (Table IV) the positive shift of the band near 1450 cm^{-1}, as strong as in square-planar complexes[4], points to a remarkable increase of the N–C double bond character.

The absorption near 275 ± 10 cm^{-1} is attributed to ν(Fe–Se), in agreement with the value of 353 cm^{-1} for ν(Fe–S)[12] if the same force constant value is used for both linkages.

As far as the octahedral iron(III) derivatives are concerned, these compounds show anomalous magnetic moment values. In fact temperature dependence measurements of magnetic susceptibilities (summarized in Table V and graphically presented in Figure 1) for *pidsc* and *modsc* derivatives show the existence of a reversible equilibrium between low- and high-spin states

$$^6A_1 \overset{K}{\rightleftarrows} {}^2T_2$$

whose energy separation should have a value comparable with thermal energies. By contrast, in the experimental temperature range (124–370° K) the magnetic moments for *tmdsc* derivatives are practically constant although intermediate between the high- and low-spin theoretical values.

If the equilibrium constant is defined by $K = N_H/N_L$, where N_H and N_L are the molecular fractions for high- and low-spin, respectively, K values can be calculated from the experimental magnetic moments assuming $\mu = 1.732$ and $\mu = 5.916$ B.M. for the $^6A_1$ and $^2T_2$ states.

TABLE III. The Electronic Spectra of the Iron(III) Pentacoordinate Derivatives (wavenumbers in kK and logε in parenthesis).[a]

		Ligand Bands		Charge Transfer Bands					*d–d* Bands		
X	Fe(*pidsc*)$_2$Cl	36.5(4.49);	30.3(4.24)		25.2(3.73)		19.8(3.85)		14.6(3.57)	8.5	6.1
XI	Fe(*modsc*)$_2$Cl	35.9	30.3	28.7sh	25.3				14.6		
XXI	Fe(*modsc*)$_2$Br[b]	35.0(4.29);		27.6sh	24.3(3.70)		19.5(3.71)	19.0sh	14.5(3.49)	7.4	
XXII	Fe(*modsc*)$_2$I	33.2(4.59)		27.6(4.37)	24.3sh	22.5sh	19.6(3.71)	17.8sh	14.5(2.52)		
XXIII	Fe(*tmdsc*)$_2$Cl	35.7	29.3	28.7sh	25.3				14.6		
	Fe(*Et$_2$dsc*)$_2$Cl[c]	35.4sh (4.16);	32.2(4.10)	28.2sh	26.0sh (3.63);	22.0(3.60)			16.2	8.4	6.5

[a] All spectra were recorded in CH_2Cl_2 solutions. [b] Another maximum was observed at 40.65(4.47)kK. [c] Ref. 13.

TABLE IV. The Most Important Infrared Absorptions in the Square-pyramidal and Octahedral Complexes.[a]

		Approximate Description									
		ν(CN)+δ(CH$_2$)			ν(CNC)+ν(CSe$_2$)		ν(CSe$_2$)			ν(M–Se)	ν(M–Cl)
		cm^{-1}	Δ	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	Δ	cm^{-1}		
	pidsc	1473s	–	1425s	851m	830s	510m	–	370m	–	–
X	Fe(*pidsc*)$_2$Cl	1520vs	+47	1438s	850m	840w	472m	–38	–	285s	311vs
XII	Fe(*pidsc*)$_3$	1480vs	+7	1427s	855m	822ms	475w	–35	–	267m 237m	
XV	Co(*pidsc*)$_3$	1478vs	+5	1432vs	845m		471w	–39	–	304–299m	
XVIII	Cr(*pidsc*)$_3$	1488vs	+15	1430s	853sh	849vs	475m	–35	–	291s	
	modsc	1445s	–	1415s	854m	835s	519m	–	366m	–	
XIII	Fe(*modsc*)$_3$	1480vs	+35	1422s	865s	840sh	485m	–34	–	273m 233m	
XVI	Co(*modsc*)$_3$	1480vs	+35	1428vs	862ms		498m	–21	–	304–299m 270m	
XIX	Cr(*modsc*)$_3$	1475vs	+30	1425vs	863m	850w	482m	–37	–	290s	
	tmdsc	1467s	–	1413s	856s		507m	–	375w	–	
XIV	Fe(*tmdsc*)$_3$	1470vs	+3	1430s	855ms		–	–	–	267s 233s	
XVII	Co(*tmdsc*)$_3$	1472vs	+5	1432s	872m		–	–	–	304w 233m	
XX	Cr(*tmdsc*)$_3$	1475vs	+8	1429s	875s	842w	–	–	–	292ms	

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

TABLE V. Dependence of Magnetic Moment Values (B.M.) on Temperature for Iron(III) Derivatives.

Fe(*pidsc*)$_3$		Fe(*modsc*)$_3$		Fe(*tmdsc*)$_3$		Fe(*pidsc*)$_2$Cl	
T°K	μ	T°K	μ	T°K	μ	T°K	μ
173	2.05	124	2.70	131	1.97	138	3.79
182	2.12	132	2.80	141	1.93	142	3.90
192	2.14	142	2.86	151	2.01	152	3.90
202	2.16	152	2.95	161	2.00	162	3.89
211	2.17	160	3.02	171	1.98	172	3.90
212	2.10	171	3.06	181	1.98	182	3.89
221	2.12	181	3.17	191	2.00	192	3.89
231	2.13	191	3.20	201	1.99	212	3.91
241	2.27	201	3.28	210	1.96	222	3.89
261	2.15	210	3.28	220	1.96	231	3.91
300	2.24	220	3.33	230	2.00	241	3.90
310	2.26	230	3.36	240	1.96	251	3.89
320	2.28	240	3.39	250	1.90	261	3.90
330	2.29	250	3.41	270	1.98	280	3.90
339	2.32	260	3.42	280	1.97	290	3.88
		270	3.43	290	1.98	298	3.89

A plot of lnK *versus* 1/T produces a straight line for both Fe(*pidsc*)$_3$ and Fe(*modsc*)$_3$*.

ΔH values of 360 (126 cm^{-1}) and 400 cal mol^{-1} (140 cm^{-1}) are thereby obtained, the positive signs showing that the ^{6}A$_1$ state is preferred at low temperature. These values are of the same order of magnitude as the thermal energies so that different ^{6}A$_1$ and ^{2}T$_2$ populations originate by small temperature changes.

A similar electronic equilibrium between the same ^{6}A$_1$ and ^{2}T$_2$ states has been identified for many iron(III) dithiochelates[14] while for Fe(*pidtc*)$_3$ and Fe(*modtc*)$_3$ complexes values of μ = 4.01 and μ = 4.03 B.M. (at room temperature) are reported[15]. Thus it is clear that in our *dsc* derivatives the equilibrium is more shifted towards the low-spin state than in the corresponding dithiocarbamates.

The electronic spectra, very poor in absorptions, are reported in Table VI. Together with the ligand–ligand transitions, bands probably *d–d* in character lie at 16.5 and 14.3 (shoulder) kK. In the infrared region

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* Straight line parameters: Fe(*pidsc*)$_3$, intercept –1.332; slope –179.1; r = 0.982; Fe(*modsc*)$_3$, intercept + 0.427; slope –199.8; r = 0.997.

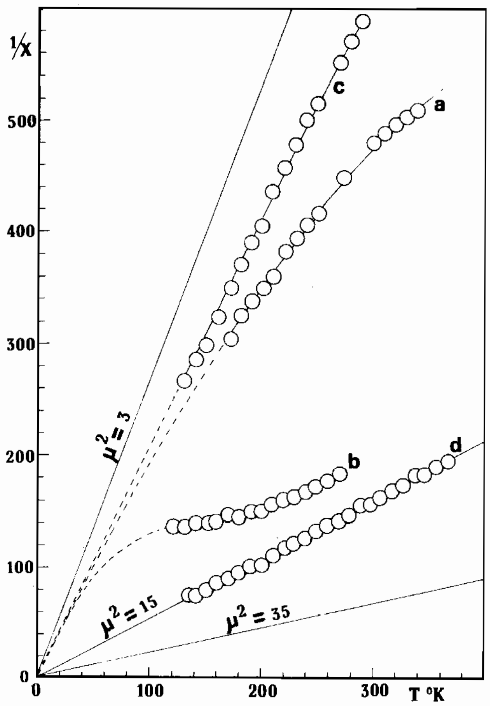

Figure 1. Magnetic behaviour of the iron(III) diselenocarbamates: (a) Fe(*pidsc*)$_3$; (b) Fe(*modsc*)$_3$; (c) Fe(*tmdsc*)$_3$; (d) Fe(*pidsc*)$_2$Cl. The straight lines indicate the theoretical trends for one, three or five unpaired electrons, respectively.

(Table IV) the positive shifts of the ν(CN) are of about 3–7 cm^{-1} for *pidsc* and *tmdsc* and of about 35 cm^{-1} for *modsc*. In every case this shift is less marked in these octahedral complexes than in the others. Two well defined new absorptions near 270 and 230 cm^{-1} can be attributed to Fe–Se vibrations, coherently with the values of 365 and 320 cm^{-1} found for Fe–S$_6$ environments[14].

Chromium(III) and Cobalt(III) Derivatives

The green chromium(III) diselenocarbamates are obtainable by refluxing the reactants overnight and are purified by TLC. Together with the ligand-to-ligand, ligand-to-metal and metal-to-ligand charge transfer absorptions (see Table VI), two of the three transitions allowed are defined, ν_1 ($^4T_{2g}\leftarrow{}^4A_{2g}$) at 14.7 kK and ν_2 ($^4T_{1g}(F)\leftarrow{}^4A_{2g}$) at 18.7 kK. ν_3 ($^4T_{1g}(P)\leftarrow{}^4A_{2g}$), covered by the stronger charge transfer bands, can be calculated by means of the ν_1 and ν_2 values and to occur at 30.9–31.4 kK. Racha's B parameter and the ratio B/B° $= \beta$[16] are respectively 370–400 cm^{-1} and 0.40–0.43, pointing to a marked nephelauxetic effect for selenium atoms in octahedral environments, in accordance with the series of donor atoms[17],

$$F > O > N > Cl > Br > S \simeq I > Se.$$

Starting from the cobalt(II) chloride the diamagnetic, brown cobalt(III) diselenocarbamates are obtained, even when working in a nitrogen atmosphere; only in the case of *modsc* is a green hygroscopic product present together with the brown Co(*modsc*)$_3$.

For an $^1A_{1g}$ ground state two spin-allowed transitions are expected, ($^1T_{2g}\leftarrow{}^1A_{1g}$) and ($^1T_{1g}\leftarrow{}^1A_{1g}$), together with two weak bands at lower energies due to the spin-forbidden, *i.e.* singlet–triplet, transitions ($^3T_{2g}\leftarrow{}^1A_{1g}$) and ($^3T_{1g}\leftarrow{}^1A_{1g}$). We observe two bands at 14.3 and 12.9 kK respectively with ε values ranging between 300 and 800 mol^{-1} cm^2, while the first of the spin-forbidden transitions lies at 10.4 kK ($\varepsilon \cong 10$). From these assignments B and C results as 157–160 and 1950–2000 cm^{-1} respectively and the β value is 0.14–0.15 (using for the free cobalt(III) ion a B° value of 1100 cm^{-1}).

The Δ value of 12.35 kK is of course coherent with that of 15.5 obtained for Co(*dtc*)$_3$ and the resulting selenium position in the spectrochemical series is slightly lower than sulphur.

Using the lowest charge transfer value the selenium optical electronegativity can be evaluated[18]. The results are 2.42 from the chromium and 2.68 from the cobalt derivatives. The average value of 2.55 is in good agreement with the previously reported data[13].

In the far infrared region (Table IV) the band at 304 cm^{-1} for the cobalt and at 291 cm^{-1} for the chro-

TABLE VI. Electronic Spectra of the Octahedral Complexes (wavenumbers in kK, logε in parentheses).[a]

	C.T.		Ligand Bands		C.T.	*d–d* Bands		
Fe(*pidsc*)$_3$			35.4(4.99)	31.8(4.80)				
Fe(*modsc*)$_3$			34.1(4.69)	28.4sh	22.5sh	16.5(3.13)	14.3sh	
Fe(*tmdsc*)$_3$			34.2(4.95)	31.9sh	28.8sh	16.4(2.89)	14.3sh	
Co(*pidsc*)$_3$	38.6(4.43)	37.5(4.43)	32.5(4.50)	28.4(4.31)	24.3(4.12)	14.3(2.83)	12.9(2.50)	10.5(1)
Co(*modsc*)$_3$	38.7(4.61)	37.0sh	31.8(4.65)	28.0(4.37)	24.3(4.12)	14.3(2.80)	12.9(2.37)	10.5(1)
Co(*tmdsc*)$_3$	39.0(4.52)	36.5(4.55)	32.2(4.56)	28.1(4.31)	24.1(4.16)	14.5(2.78)	12.9(2.50)	10.5(1)
Cr(*pidsc*)$_3$	38.6sh		34.2sh	33.0(4.58)	27.8(4.29)	18.7(2.64)	14.7(2.69)	
Cr(*modsc*)$_3$	38.6sh		34.2sh	32.9(4.73)	27.6(4.49)	18.7(2.60)	14.7(2.79)	
Cr(*tmdsc*)$_3$	37.6sh		34.0sh	32.8(4.59)	27.6(4.26)	19.1(2.62)	14.8(2.68)	

[a] All spectra were recorded in CH$_2$Cl$_2$ solution.

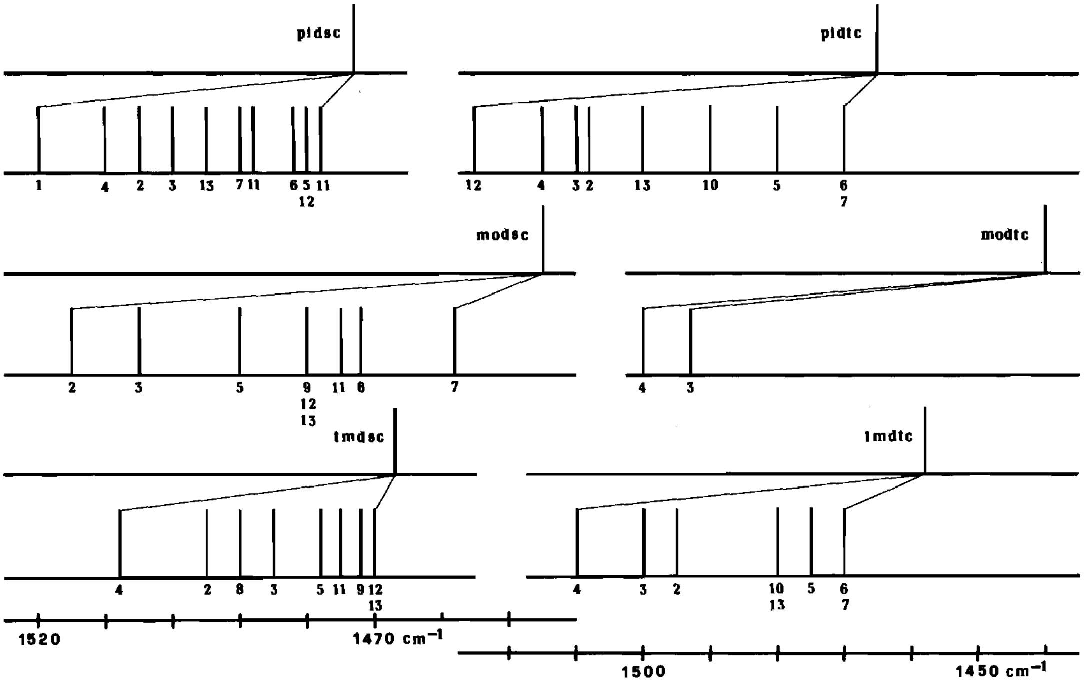

Figure 2. Positive shifts of ν(C—N) on going from the free ligands to the complexes (*dtc* values from refs. 15 and 19). 1) FeL_2Cl; 2) NiL_2; 3) PdL_2; 4) PtL_2; 5) ZnL_2; 6) CdL_2; 7) HgL_2; 8) $HgLCl$; 9) CoL_3; 10) CoL_2; 11) CrL_3; 12) FeL_3; 13) CuL_2.

mium complexes is due to metal–selenium stretching. Taking into account the wavenumber order and the reduced mass values, the metal–selenium force constant seems to vary in the order $Co > Cr \geqslant Fe$. As far as the ν(CN) wavenumbers are concerned, these increase with coordination by about ten cm^{-1}, pointing to some increase of double N–C bond character. Comparing this result with those reported earlier for square-planar[4], tetrahedral, square-pyramidal or octahedral environments for *dtc*[15,19] and *dsc* complexes we observe (see Figure 2): (i) The N–C double bond character is nearly the same in the complexes, being increased more in the *dtc* than in the *dsc* series; (ii) This character is the highest in the iron(III) square-pyramidal derivatives; (iii) The trend is roughly the following:

$$\underbrace{Fe}_{\text{square pyram.}} > \underbrace{Pt > Ni \simeq Pd}_{\text{square planar}} > Cu \simeq \underbrace{Hg > Cd > Zn}_{\text{tetrahedral}} \simeq \underbrace{Cr > Fe > Co}_{\text{octahedral}} > \text{free ligand}$$

confirming some previously reported results[20].

The green product accompanying the Co(*modsc*)$_3$ complex was not so well defined as a consequence of its great instability and hygroscopicity. It seems to be *mo*H[Co(*modsc*)$_3$] (Calcd. C%, 24.9; found 24.8), paramagnetic and 1:1 electrolyte. In its i.r. spectrum the typical bands of the *mo*H$^+$ cation are present as well as those of *modsc* derivatives.

Experimental

Preparation of the Complexes

The preparation of the ligands was described earlier[4]. All complexes were obtained by double exchange reaction in aqueous solution between the stoichiometric amount of the metal chloride and the ligand internal salt *(i.e., piHpidsc, moHmodsc, tmHtmdsc)* at room temperature; for chromium derivatives only the reaction was carried out by refluxing overnight at 100° C. The crude products were purified by recrystallization or TLC. Analytical data and some physical properties are reported in Table I.

Spectrophotometric Measurements

The electronic spectra were recorded with a Pye Unicam SP 700 C and with a Perkin–Elmer 402 spectrophotometer in CH_2Cl_2 solutions in the range 40.000–5.000 cm^{-1}. The ir spectra were carried out with a Perkin–Elmer 325 instrument in the range 4.000–200 cm^{-1} as KBr discs or nujol mulls between CsI plates.

Magnetic measurements

These measurements were carried out by Gouy's method with a Newport instrument in nitrogen atmosphere.

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