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Electronic Spectra of Some Isocyanide Complexes

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The isoelectronic complexes with O_h symmetry $Fe(CH_3NC)_6Cl_2 . 3H_2O$ and $Mn(CH_3NC)_6I$ have been investigated according to the SCCC–MO method with the aim of interpreting the electronic spectra. Qualitative correlations among electronic properties of these compounds and the vibrational and NMR spectra are proposed.

Introduction

The electronic properties of some hexacarbonyl and hexacyanometallates of the transition metals have been investigated by semiempirical MO calculations.[1,2] However, analogous investigations are lacking for the hexaisocyanide complexes, many of which are reported in the literature and which show similarities to hexacyanometallates and hexacarbonyls.

Thus, it seems interesting to examine the electronic properties of some of the simplest hexaisocyanide complexes by semiempirical calculations. An investigation of the isosteric complexes $Fe(CH_3NC)_6Cl_2 . 3H_2O$ and $Mn(CH_3NC)_6I$, utilising semiempirical SCCC–MO calculations, is reported in this paper. Correlations among electronic properties and vibrational and NMR spectra of these compounds are proposed on the basis of the results of the electronic population analysis. The only structure[3] solved by X-rays to date is $Fe(CH_3NC)_6Cl_2 . 3H_2O$, its idealized symmetry is O_h and the Fe–C lengths are 1.85 Å, a value which has been utilized in the calculations. The symmetry of $Mn(CH_3NC)_6I$, which presents IR and Raman spectra with the same number of ν(N–C) (see Table I), according to vibrational analysis for O_h symmetry (A_{1g}(R); E_g(R); T_{1u}(IR)), has been assumed to be O_h analogous to that of the Fe^{II} compound. Distances Fe–C have been transferred to the manganese compound, because of the lack of experimental values for Mn–C bonds. This transfer is supported by the fact that the metal-carbon distances, on passing from the Fe^{II} compound to the Mn^I, should vary by only a few hundredths of Å, which would have a negligible effect on the atomic overlaps. Furthermore, this approximation is often accepted in the investigation of the electronic structure of a series of analogous compounds,[1] since, when the structural data are available, the variations are of same order as the precision of the data.

No SCF calculations have been carried out on the CH_3NC ligand due to the unavailability of spectroscopic data for the determination of M.O. energies. This is because of the induced isomerisation of RNC to RCN by UV light.[25] These energies are necessary for obtaining an eigenfunction as good as those obtained for other carbon ligand. For CH_3NC only the I.P. is known.[26]

For this reason only the metal ion 3d, 4s, 4p, and pure carbon 2s and 2p orbitals can be taken as a basis for the calculation. Such a high degree of approximation, which has been used earlier,[4,5] does not distinguish the electronic structure of the CH_3NC ligand from the structures of the other carbon ligands. However, we believe that our calculations are still of some value as the electronic structure of isocyanide complexes calculated by us suggest a significant interpretation of some experimental spectroscopic data. This restricted basis for the calculation, which is very useful since it reduce the dimensions of the problem, give rise to several inconveniences, for instance the impossibility of giving a precise meaning to the antibonding orbitals (π^*_L) of the ligand, in which the back-donating electrons are placed. We have overcome this difficulty by doubling the symmetry functions constructed whith the p_π orbitals of the carbon, thus treating the first of the two functions as a π^b orbital of the ligand and the second as a π^* orbital.

This obviously introduces a simplification since in this way it is assumed that carbon has equal weight in the formation of π^b and π^* orbitals.

An energy value for the 2s orbitals of the carbon close to that proposed by Gray for hexacyanometallates and hexacarbonyls,[1] has been chosen. The energies of $2p_\sigma$ and $2p_\pi$ orbitals have not been differentiated empirically,[6] but according to the value of the correction term of the internal overlap of the symmetry functions.[7] The value of 85 kK, which allows fitting of the experimental C.T. band, has been chosen for the energy difference between the 2p orbitals of π^b type and π^* type of the carbon atom. Slater orbitals have been used to compute overlap integrals as suggested by Zerner *et al.*[8] The energies of the metal orbitals, VSIE,[9] calculated as a function of charge and configuration, and those of the ligand are reported in Table II.

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Table I. IR and Raman spectra (2500-200 cm^{-1}).

$Fe(CH_3NC)_6Cl_2 . 3H_2O$		$Mn(CH_3NC)_6I$		Symmetry	Description
IR [a, c]	Raman [b]	IR [a,c]	Raman [b]		
—	2272.5 s	2220 vw [a]	2216 m	A_{1g}	νCN
—	2240 vs	—	2150 vs	E_g	νCN
2229 vs [a]	—	2115 s [a]	—	T_{1u}	νCN
1640 w [a]	1640 vw	—	—	—	δHOH
—	1450 sh	—	1450 vw	—	$\delta_{as}CH_3$
—	1420 sh	—	—	—	?
1410 w [a]	1415 s	1408 m [a]	1412 s	—	δ_sCH_3
—	—	—	1130 vw	—	rock.CH_3
975 w [a]	950 w	950 w [a]	970 w	—	νCH_3-N
600 m(br)	625 vw	—	—	—	ʃH_2O
562 s [c]	—	586 s [c]	—	T_{1u}	δNCMe
—	500 m	—	—	T_{2g}	δNCMe
—	—	472 w [c]	—	—	?
370 m [c]	370 vvw	380 m [c]	—	T_{1u}	νMe-C
—	300 w	—	360 w	—	νMe-C ?
—	—	—	295 m	—	δCH_3NC
230 m [c]	236 ?	—	—	—	δCH_3NC ?

[a] in KBr; [b] in solid; [c] in nujol; ʃ wagging or rocking mode (24).

Table II.

	Metal VSIE (kK)			Metal configuration			Metal charge
	4s	4p	3d	4s	4p	3d	
$Fe(CH_3NC)_6^{2+}$	82.440	49.477	100.076	0.0228	0.0172	7.3619	0.5981
$Mn(CH_3NC)_6^{+}$	81.487	49.487	97.818	0.0158	0.1281	6.2653	0.5908

	Ligand VOIP (kK)			Ligand configuration				Ligand Charge
	2s	2p	π*	s	p_σ	p_π	π*	
$Fe(CH_3NC)_6^{2+}$	160.000	135.000	50.000	1.8975	1.7458	3.9663	0.1748	0.2336
$Mn(CH_3NC)_6^{+}$	160.000	135.000	50.000	1.8370	1.7787	3.9453	0.3708	0.0682

	F_σ	F_π
$Fe(CH_3NC)_6^{2+}$	1.61	2.15
$Mn(CH_3NC)_6^{+}$	1.55	2.30

The resonance integrals have been calculated according to the formula:

$$H_{ij}=\tfrac{1}{2}F(\sigma,\pi)S_{ij}(H_{ii}+H_{jj})$$

with values of parameters F_σ and F_π, chosen to reproduce the electronic spectra, reported in Table II. The population analysis has been performed according to the Mulliken method,[10] modified as suggested by Dahl.[11] The whole overlap population between 4s and 4p metal orbitals and ligand orbitals is assigned to the ligand. The iterative procedure has been performed until self-consistency of charge and electronic population of the metal atom.

Electronic Spectra

The spectra of the two compounds, recorded in ethanol solution, reported in Table III, show two unresolved bands, which may definitely be assigned to the spin-allowed but Laporte forbidden d–d transitions from the ground state t_{2g}^6 ($^1A_{1g}$) to the monoexcited state $t_{2g}^5e_g$ ($^1T_{1g}$, $^1T_{2g}$). There is also a high intensity band which may be assigned to C.T. The values 10Dq=32.85 kK (Fe^{II}) and 10Dq=32.69 kK (Mn^I) are obtained from the experimental frequencies of d–d transitions neglecting second-order contributions and utilising the well known relations of the crystal field:[12]

Table III. Electronic Spectra in Ethanol Solution.

	kK	Logε	Assig.
$Fe(CH_3NC)_6^{2+}$	31.25	2.8	d-d
	37.60	2.8	d-d
	48.80	4.8	C.T.
$Mn(CH_3NC)_6^{+}$	31.25	sh	d-d
	37.00	sh	d-d
	43.10	4.6	C.T.

$$E(^1T_{1g}\leftarrow{}^1A_{1g})=10Dq-C$$

$$E(^1T_{2g}\leftarrow{}^1A_{1g})=10Dq+16B-C$$

with C=4B.[13]

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(13) C. K. Jørgensen Oxidation Numbers and Oxidation States Springer-Verlag 1969, pag. 103.

Table IV.

	MO	Energy(kK)	Eigenvector
$Fe(CH_3NC)_6^{2+}$	$2t_{2g}$	-91.499	$-0.9236(3d\pi)+0.4164(\pi_L)-0.1863(\pi_L^*)$
	$3e_g$	-58.678	$-0.9155(3d_\sigma)+0.4963(s_L)+0.7344(p_{\sigma_L})$
	$2t_{2u}$	-37.416	$1.0000(\pi_L^*)$
	$4t_{1u}$	-24.701	$0.0482(4p)-0.3772(s_L)-0.2977(p_{\sigma_L})+0.2275(\pi_L)+0.9755(\pi_L^*)$
	10Dq calc. = 32.821 kK		
	C.T. calc. = 54.083 kK		
$Mn(CH_3NC)_6^+$	$2t_{2g}$	-89.738	$0.8431(3d_\pi)-0.3902(\pi_L)+0.3787(\pi_L^*)$
	$3e_g$	-56.947	$-0.9810(3d_\sigma)+0.5131(s_L)+0.6868(p_{\sigma_L})$
	$2t_{2u}$	-46.411	$1.0000(\pi_L^*)$
	$4t_{1u}$	-30.411	$0.1279(4p)-0.4847(s_L)-0.3547(p_{\sigma_L})+0.2471(\pi_L)+0.9246(\pi_L^*)$
	10Dq calc. 32.791 kK		
	C.T. calc. = 43.327 kK		

Table IV reports energy values of some molecular levels of spectroscopic interest together with the corresponding eigenvectors. An important result of our calculations is that it gives for the electronic transition $t_{2g}^6 \rightarrow t_{2g}^5 e_g$, a value very close to 10Dq, obtained from the electronic spectrum. According to our calculations, the high intensity bands are assigned to C.T. from the metal to the ligand orbitals π^* ($t_{2g} \rightarrow t_{2u}$). Both the transitions $t_{2g} \rightarrow t_{1u}$ and $t_{2g} \rightarrow t_{2u}$ should be symmetry allowed and, as shown by the calculations on octahedral complexes,[1] the first of these should appear less intense and at lower energy than the second band. However, the unresolved, room temperature spectra recorded shows only one, very intense, band, which is probably associated with the energy difference between the metal orbitals t_{2g} and the ligand t_{2u}. The calculated values of charge and electronic configuration corresponding to the convergent calculations are reported in Table II.

The values of the charges on the metal atoms are rather small, according to the electroneutrality principle ef Pauling, and decrease slightly on going from Fe^{II} to Mn^I. A similar trend is shown by the fractional charges (Z_{root}) calculated, according to Jørgensen,[14] through on the analysis of the interelectronic repulsion parameter B from the observes d–d transitions.

The agreement in the trend of the charges between these two methods of calculations is not casual and shows that our results are chemically meaningful.

IR and NMR Spectra. The IR spectra show the trend ν(Fe–C) > ν(Mn–C) for the stretching frequencies ν(M–C). Thus it appears useful to compare the overlap populations with these frequencies. Because of the method of population analysis used and of the dimension of the atomic basis set, this comparison has to be restricted to the M–C bonds and to the 3d metal orbitals. ●However, the calculations show, notwithstanding the approximation of a restricted basis, that the shift of the (M–C) frequency in the compounds investigated is related mainly to the change of π contribution to the electronic density of the bonding (see Table V).

Table II shows that the population of the π* ligand orbitals, a measure of the back-donating power of the metal, increases on going from the Fe^{II} compound to the Mn^I one This may explain the decrease of the ν(C–N) stretching frequency passing from the Fe^{II} compound to the Mn^I one. In fact, an increase of the π* orbital population corresponds to a decrease of the C–N bond order and hence to a decrease of the corresponding stretching frequency.

The NMR spectra in CD_3OD of the CH_3NC ligand and of the two compounds show a noticeable change in the chemical shift of the methyl protons in the order $\delta_{lig} < \delta_{Mn^I} < \delta_{Fe^{II}}$.

This trend may be correlated to the value of the positive charge on the ligand.

An increase of the positive charge on the ligand should be paralleled by a decrease of the magnetic field of the protonic resonance. The results of our calculations for the values of the net charges on the ligand qualitatively confirm the observed trend in the NMR spectra (Table V).

Paramagnetic Isocyanide Complexes. We have carried out a calculation for the complex ions $Mn(CH_3NC)_6^{2+}$ and $Fe(CH_3NC)_6^{3+}$ with the approximation used for d^6 complexes and, also, similar F parameter values. This calculation gave the results shown in Table VI.

The values of the energies of the molecular orbitals of $Fe(CH_3NC))_6^{3+}$ indicate that the $3t_{1u}$ (σligand) level in this compound should have virtually the same energy as the $2t_{2g}$ (π metal) level, *i.e.* that this ion should have the $3t_{1u} \rightarrow 2t_{2g}$ charge transfer as the ground state. Because of this the optical electronegativity of the Fe^{3+} ion and of methylisocyanide, and, consequently, their ionisation potentials, would have pratically the same value. For the $Mn(CH_3NC)_6^{2+}$ ion, however, a 10Dq value of ca. 34 kK and a charge transfer (L→M) of ca. 14 kK are predicted. In a previous article[15] we analysed the electronic spectrum of $Mn(CH_3OC_6H_4NC)_6(NO_3)_2$, which, although having an aromatic isocyanide as a ligand, should exhibit both d–d and C.T. bands with values very close to those proposed in Table VI. In fact, for this compound, a band at 15.4 kK (ε = 6230) was observed, which was assigned to a L→M C T., whereas the d–d bands were not observed being covered by internal ligand transitions.

From the value of the C.T. band calculated for the Mn^{II} complex (corrected for the variation of SPE, with a B value similar to that calculated for the hexacyanides[1]) and $\chi_{opt}(Mn^{2+}) = 1.8$, obtained assuming for

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(14) Ibidem, pag. 110

(15) V. Valenti, A. Sgamellotti, F. Cariati, L. Naldini, *Ric. Sci.*, **38**, 1230 (1968).

Table V. Population Analysis, IR and NMR data.

	ν(C-N)	π* ligand population	ν(Me-C)	metal-carbon overlap population σ	π	σ+π
$Fe(CH_3NC)_6^{2+}$	2229	0.1748	370	1.0020	0.0818	1.0838
$Mn(CH_3NC)_6^{+}$	2115	0.3708	380	1.0224	0.5328	1.5552

	δ(ppm)	ligand charge
$L=CH_3NC$	2.73 [a]	0.0000
FeL_6^{2+}	2.77	0.0682
MnL_6^{+}	3.63	0.2336

[a] neat liquid, from reference 20.

Table VI.

	M.O.	Energy	Occup. Numbers	10Dq calc.	C.T. calc.
MnL_6^{+2}	$3t_{1u}$	—110.514	6	34.185	14.407
	$2t_{2g}$	— 96.107	5		
	$3e_g$	— 61.922	0		
FeL_6^{3+}	$2t_{2g}$	—102.605	6	~ 36.000	~ 0.000
	$3t_{1u}$	—102.497	5		
	$3e_g$	— 66.739	0		

	Metal configuration 4s	4p	3d	Ligand configuration s_L	p_{σ_L}	π_L	π_L^*
MnL_6^{2+}	0.0168	0.0282	6.2564	1.8889	1.7920	3.9597	0.1424
FeL_6^{3+}	0.0286	0.0003	7.9048	1.8817	1.6592	3.8940	0.0762

	Metal charge	Ligand Charge	F_σ	F_π
MnL_6^{2+}	0.6985	0.2170	1.53	1.90
FeL_6^{3+}	0.0663	0.4889	1.57	1.90

$3d^n$ ions variations in χ_{opt} similar to those of $5d^n$ ions,[61] a value of $\chi_{opt}=2.2$ is calculated for the isocyanide. This value for the optical electronegativity would indicate that isocyanide may be more reducing in character than any other ligands. We can attempt an explanation of the fact that the isocyanide complexes of the type $Fe(RNC)_6^{3+}$ and $Fe(ArNC)_6^{3+}$ have not been observed. From $\chi_{opt}(Fe^{3+})=2.1$ obtained from the literature[17] and which may, also, be increased for stabilisation of the t_{2g} orbitals due to the back-bonding capacity of the ligand; it may be deduced that the existence of this complexes is highly improbable. In fact while a difference in electronegativity between ligand and metal is not a sufficient condition for the existence of a complex, it is without doubt true that there is a lower limit to this difference if the compound is to exist. Experimentally no complexes having a charge transfer state as ground state are known.[18] The charge calculated, much smaller for the Fe^{III} complex compared with Mn^{II}, is proof that the reducing power of isocyanide is greater with Fe^{III} than with Mn^{II} (the compounds of which are stable in the presence of strong oxidants[19]), thus lowering the possibility of formation of complexes of type $Fe(RNC)_6^{3+}$.

Experimental Section

The compounds $Fe(CH_3NC)_6Cl_2 \cdot 3H_2O$ and $Mn(CH_3NC)_6I$ were prepared according to the literature.[21,22,23] IR spectra were recorded on a Perkin Elmer mod. 621 spectrometer (2500-400 cm^{-1}) and on a Hitachi P.E. mod. FIS3 spectrometer (400-200 cm^{-1}). Raman spectra were recorded on a Coderg PHO type spectrometer, electronic spectra on a Beckman DK2A spectrophotometer and NMR spectra on a Perkin Elmer R10 (60 MHz) spectrometer.

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