THE ELECTRONIC STRUCTURE OF ISOCYANIDE LIGANDS AND THE SPECTROSCOPIC BEHAVIOUR OF Mn^{II} OCTAHEDRAL COMPLEXES

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Summary

A correct description of the nature of transition metal isocyanide complexes is strictly related to the knowledge of the electronic structure of the ligands and we have therefore carried out extensive MO—LCAO—CNDO calculations for a series of isocyanides. Furthermore, the spectroscopic assignments of some octahedral Mn^I and Mn^{II} isocyanide complexes are revised with a view to interpreting magnetic, optical and electronic properties. General correlations are made between the π accepting ability, the ionization potential, the optical electronegativity of the different ligands and the stability towards reduction of the corresponding Mn^{II} complexes.

Introduction

In the last few years interest in the inorganic and organic chemistry of isocyanides has been renewed [1,2] and isocyanide complexes of all the transition metals have been reported, but their electronic structure has been the subject of very few investigations [3,9]. Strangely, the electronic structure of free isocyanide has never been investigated in great detail neither has the effect of the different substituents bound to isocyanide group been discussed theoretically. Consequently the structure of isocyanides either free or coordinated to a metal are still described in terms of a combination of canonical formulae with a Valence Bond approach, which is definitely an inadequate theoretical model [10]. Moreover the substituent effects have been usually extrapolated in an arbitrary way. Some MO—LCAO [11,15] calculations on free isocyanides have been reported but, since few molecules have been investigated and different approximations have been used, it has been difficult to formulate correlations between chemical and electronic properties.

The aim of this work is to present a semiempirical MO—LCAO investiga-

tion of a complete series of isocyanides and to describe how some properties of free isocyanides determine the chemical and spectroscopic behaviour of the complexes.

To support this thesis we have studied the vibrational and the electronic spectra of the Mn^{II} hexacoordinated octahedral complexes whose interpretation is still not well defined.

Results and discussion

The electronic structure of the isocyanides

We have carried out MO—LCAO—CNDO [16,17] calculations for the molecules, CH_3NC, C_2H_5NC, C_2H_3NC, C_6H_5NC, p-$CH_3C_6H_4NC$ and p-$CH_3OC_6H_4NC$. Methyl isocyanide, whose geometrical structure [18], dipole moment [19] and first and second ionization potential [20] are known, is discussed in more detail than the other compounds.

The results obtained for methylisocyanide partially agree with those obtained by ab initio calculations [13]. Assuming C_{3v} symmetry the results of our calculations give the ground state as $(1a_1, 2a_1, 3a_1)^6 4a_1^2 5a_1^2 6a_1^2 1e^4 7a_1^2$. The occupied molecular orbital of highest energy $(7a_1)$, in agreement with photoelectron spectroscopy results [20], is associated with the carbon atom lone-pair and its energy, —15.5532 eV, can be compared to the first ionization potential of 11.27 eV. The $2e$ molecular orbital contains important contributions from the atomic orbitals of the NC group with π-symmetry and has an energy of – 16.1899 eV as compared with the second ionization potential of 12.24 eV. These results thus show that the CNDO method gives in general higher absolute values for the orbital energies than the experimental values, but, still, we believe that this method of calculation is of some validity when the results obtained are used as a basis for comparison of some electronic properties within a series of similar molecules.

The calculated electronic populations (see Table 1) are notably different from those obtained by ab initio calculations [12,13]; despite this our calculated dipole moment is equal to the experimental value of 3.83 D and is better

TABLE 1

ELECTRON POPULATION IN CH_3NC MOLECULE

		Present work	From ref. 13	From ref. 12
C(CN)	s	1.660	1.592	3.607 (1s + 2s)
	p_σ	1.101	1.121	1.078
	p_π	1.366	1.147	1.206
	Net charge	—0.127	0.140	0.113
N	s	1.254	1.285	3.390 (1s + 2s)
	p_σ	1.115	1.233	1.218
	p_π	2.621	2.855	2.810
	Net charge	0.011	—0.363	—0.418
C(CH)$_3$	s	1.027		3.268 (1s + 2s)
	p_σ	0.910		0.809
	p_π	1.989		2.580
	Net charge	0.074		—0.657
H		0.986		0.679
	Net charge	0.014		0.321

than the ab initio value of 4.17 D. The substantial difference between the CNDO and ab initio method is that the former, in accordance with Valence Bond theory [21], and with the results of Bak and coworkers [22] provides for an important contribution from the polar form $CH_3-\overset{-}{N}-\overset{+}{C}$, whereas the latter method considers the polar form $CH_3-\overset{+}{N}-\overset{-}{C}$ to be the more important.

The chemical properties of isocyanides are related to their ability to act as π-acceptors: in order to clarify the back-donation mechanism we have performed two different types of calculations: the first describes the π-accepting ability of the ligand as a function of the relative energy of the empty orbitals of the ligands with respect to the energy of the d metal orbitals, the second, as proposed by Mc Weeney et al. [23] involves discussion of the electronic distribution and of the geometric structure of the first excited state of the ligand. According to the first approach we have calculated the variation in energy of the $2e(\pi^b)7a_1(\sigma^b)$ molecular orbitals and also of the $3e(\pi^*)$ virtual orbital as a function of the CH_3N-C distance (see Fig. 1). The bond length ranges from 1.10 Å to 1.22 Å, and is similar to that observed in the coordination compounds [9,10,20,25]. As the CH_3N-C distance increases, the energy of the $3e$ orbital approaches more closely that of the metal d orbitals and greater back-donation results. In agreement with this latter point we have a decrease of the $RN-C$ bond length (with respect to the value of the free ligand) when coordination of the isocyanide occurs with a positively charged ion or when other better π-acceptors are bound to the metal ion [e.g. in $MnBr(CO)_3(CNCH_3)_2$]. When this two facts not occur [as in $(CNCH_3)CuI$], we observe an increase of the $RN-C$ bond length.
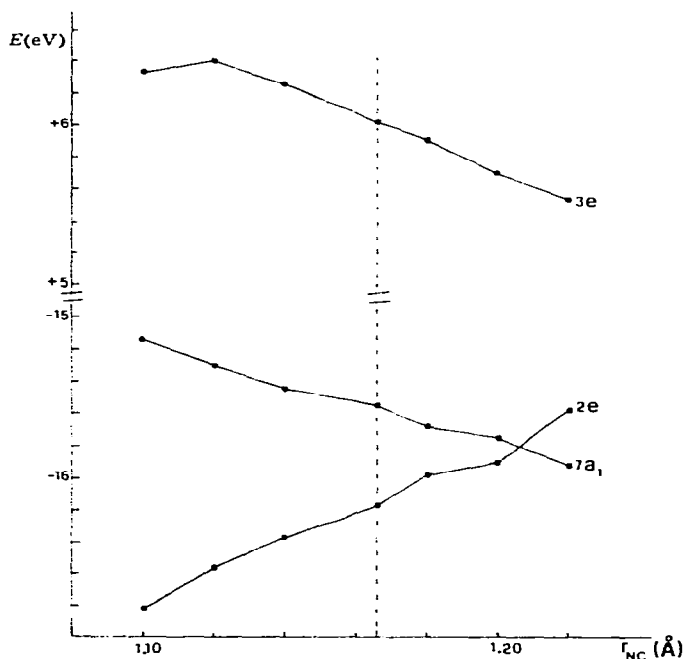

Fig. 1. Energy of the $2e$, $7a_1$ and $3e$ molecular orbitals as function of C—N distance in CH_3NC.

TABLE 2

CNDO CALCULATED GEOMETRICAL PARAMETERS, BOND-ORDER AND E_{CN} ENERGY FOR CH_3NC MOLECULE[a]

	CH_3N-C (Å)	CH_3-NC (Å)	$\angle C-N-C$	CN bond order	E_{CN} energy (eV)
Singlet ground state	1.199 (1.166)	1.390 (1.429)	180.0°	1.284	−73.846
Triplet excited state	1.229	1.387	180.0°	1.264	−65.313

[a]In parentheses experimental values from ref. 18.

TABLE 3

CNDO CALCULATED BOND LENGTHS, BOND ORDERS, E_{CN} AND DIPOLE MOMENTS FOR RNC MOLECULES[a]

R	$RN-C$ (Å)	$R-NC$ (Å)	$(B.O.)_{CN}$	E_{CN} (eV)	Dipole moment (D)
C_2H_5	1.202 (1.16[b])	1.403 (142[b])	1.280	−73.781	3.88 (3.50[c])
C_2H_3	1.204 (1.165[d])	1.376 (1.376[d])	1.270	−72.943	3.40 (3.56 ± 0.06[d])
C_6H_5	1.205	1.382	1.268	−72.922	3.59 (3.56[e])
$p\text{-}CH_3C_6H_4$	1.202	1.407	1.278	−73.394	4.29 (4.01[e])
$p\text{-}CH_3OC_6H_4$	1.20[f]	1.40[f]	1.282	−73.756	4.42

[a]In parentheses experimental values and references. [b]Ref. 38. [c]Ref. 11. [d]Ref. 38. [e]Ref. 39. [f]Assumed values.

According to the second approach, when back-donation occurs, the ligand has antibonding orbitals which are partially occupied and must be described by an eigenfunction which does not have negligible weights of the excited configurations. In methyl isocyanide the first excited configuration may correspond to the triplet (......) $2e^4 7a_1 3e$. We have determined its geometry by minimising the total molecular energy as a function of the $CH_3 N$—C and CH_3—NC bond lengths and of the C—N—C bond angle*. The results of this calculation, reported in Table 2, together with that for the analogous calculation for the singlet ground state, show that the $CH_3 NC$ molecule is always linear and that the population of the $3e$ orbital produces an increase in the $CH_3 N$—C distance but does not affect the CH_3—NC distance. It might therefore be expected that in the coordinated ligands a fairly high contribution of the excited triplet state should not produce sensible changes in the linearity of the C—N—C moiety.

This has been confirmed by structural studies on isocyanide transition metal complexes and is in contrast with the Valence Bond theory which suggests that the isocyanide bonded to strong π donor metals has the bent structure R$-\overline{\overline{N}}\gtrless$C.

Generally, the change in the geometric properties of the complexes is not the major influence upon back donation; the most evident change brought about by the back-donation appears in the bond-orders.

Such effects should be detectable in the vibrational spectra, since any shift in the C—N stretching frequency may be correlated with a variation in the electron density in the region between the two atoms. In fact, if back donation brings about partial population of the antibonding orbitals of the CN group, then it must be concluded that the greater is the back-donation, the smaller the bond order. To evaluate how back-donation could modify the C—N bond order we have calculated the strength of the C—N bond by two different methods namely, by the total bond-order indices and by the interaction energy of the C and N atoms.

According to CNDO theory, the total bond-order indices are a simple sum of the elements of the interatomic block of the density matrix. The values obtained in this way are not significant. Alternatively it has been suggested [27] that the total A—B bond order may be calculated with the aid of the overlap integrals, by the following expression:

$$(B.O.)_{A-B} = \Sigma_\mu^A \Sigma_\nu^B P_{\mu\nu} \cdot S_{\mu\nu}$$

We believe this method has little theoretical justification however, because the $P_{\mu\nu}$ elements are related to an orthogonal basis. Nevertheless this method gives better values than does the former and the trend of the total bond-order agrees with chemical expectations.

To avoid theoretical difficulties we propose to discuss the strength of the A—B bond in terms of the diatomic interaction energy. It is well known [16] that in CNDO theory the total molecular energy may be partitioned into atomic and diatomic contributions, namely:

$$E_{total} = \Sigma_A E_A + \Sigma_{B > A} E_{AB}$$

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* The optimization of the geometrical parameters has been performed with the aid of the VAO 4A routine programmed by M.J.D. Powell, QCPE Programm n. 60.

where the E_{AB} terms are functions of the elements of bond-order, overlap and coulomb interaction matrices, so that they are strongly influenced by variation in bond-length and by hybridization.

In Table 2 we list the bond-order and the E_{CN} values. It is interesting to note that the decrease of the E_{CN} value from the ground to the excited state of methyl isocyanide is large, that is, a contribution of the excited state in the coordinated ligand should be accompained by a rather large weakening of the C—N bond and by a subsequent decrease in the v(C—N) frequency.

This theory can account for the facts usually related to the back-donation mechanism but cannot, however, explain why, in some complexes the RN—C distance is shorter and the v(C—N) frequency higher than that in the free ligand. Only few structural and physical data have been reported for the other iso-cyanides, and in order to investigate their electronic configurations, we have assumed that the C—N—C group is linear, that the RN—C and R—NC distances
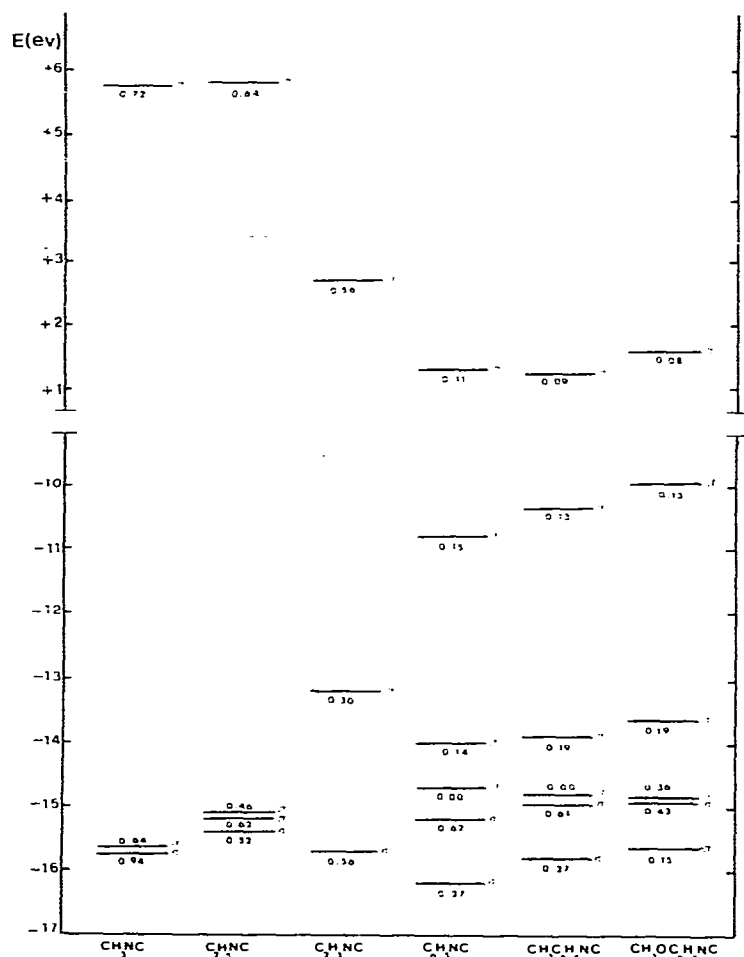

Fig. 2. Energy of MO of the RNC molecules and contributions of the π atomic orbitals of the CN group.

are those obtained by CNDO calculations minimising the total energy of the molecule. The calculated values, given in Table 3 together with the dipole moments, the bond orders and the E_{CN} values do not differ appreciably from molecule to molecule. However, in the ligand series, the differences between the energy and the compositions of the highest occupied MO(HOMO) are significantly different as can be seen from Fig. 2. Fig. 2 shows the energies of the MO's obtained by the CNDO calculations which optimize the molecular geometry.

The HOMO orbitals contain contributions from the atomic orbitals of π-symmetry of the CN group; these contributions decrease when the CN group is conjugated, and even more so when there is extensive delocalization. The energy of this MO varies greatly as a function of R (see Table 4); our calculations show that, with the exception of methyl isocyanide, the first ionization potential is affected by the π-type orbitals of the CN group and in the case of the aromatic isocyanides also by orbitals in which the prevalent contribution is from the phenyl system. This is in agreement with the proposal [27] made on the basis of experimental ionization energies.

The destabilization of the HOMO is accompanied by an increase in stabilization of the first virtual orbital (FVMO), and this explains why in general the aliphatic isocyanides are poorer π-acceptors than the aromatic isocyanides. The energy and composition of the HOMO and of the FVMO of the different molecules also underline how the nature of R notably influences the energy of the MO which interacts strongly with the d orbitals of the metal. The calculations also confirm that the polarity of the CN group corresponds to that found in the case of CH_3NC. The orbital populations and the net charge of the atoms are given in Table 5 where the numbering of the atoms is as shown in Fig. 3.

Properties and spectra of the manganese octahedral isocyanide complexes

Manganese(I) isocyanide complexes, both aliphatic and aromatic, are hexacoordinate, white in colour and diamagnetic both in the solid and in solution [33]; those of manganese(II), while also hexaco-ordinate, show different features according to the nature of the ligand [28,34]. Those with aliphatic isocyanides are light pink and, both in the solid and in solution, they exhibit a paramagnetism corresponding to low spin d^5 complexes; those with aromatic isocyanides, while exhibiting the same paramagnetism in the solid state are, however, intense blue or violet, and, which is most important, according to Matteson and Bailey [28] their solutions are diamagnetic. These authors

TABLE 4

IONIZATION POTENTIALS (eV) FOR RNC MOLECULES

R	Calcd.	Obs.	Ref.
CH_3	15.553	11.27	20
		11.80	38
C_2H_5	15.117	11.20	38
C_2H_3	13.221		
C_6H_5	11.877	9.70	28
p-$CH_3C_6H_4$	10.361	9.63	28
p-$CH_3OC_6H_4$	9.948		
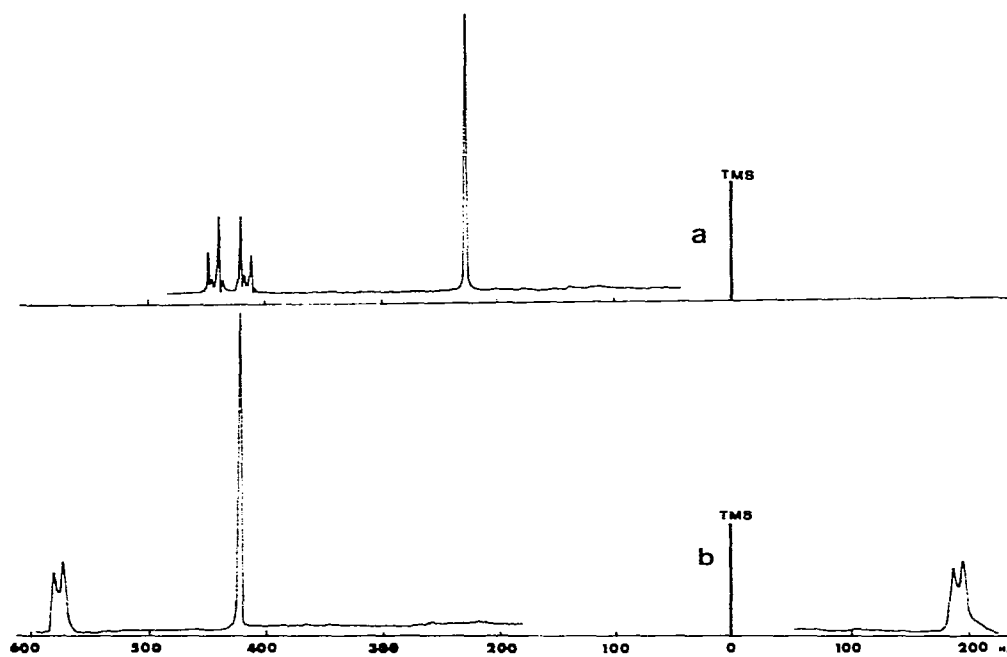
Fig. 4. PMR spectrum of a) [Mn(p-CH$_3$OC$_6$H$_4$NC)$_6$]PF$_6$ and b) [Mn(p-CH$_3$OC$_6$H$_4$NC)$_6$](PF$_6$)$_2$.
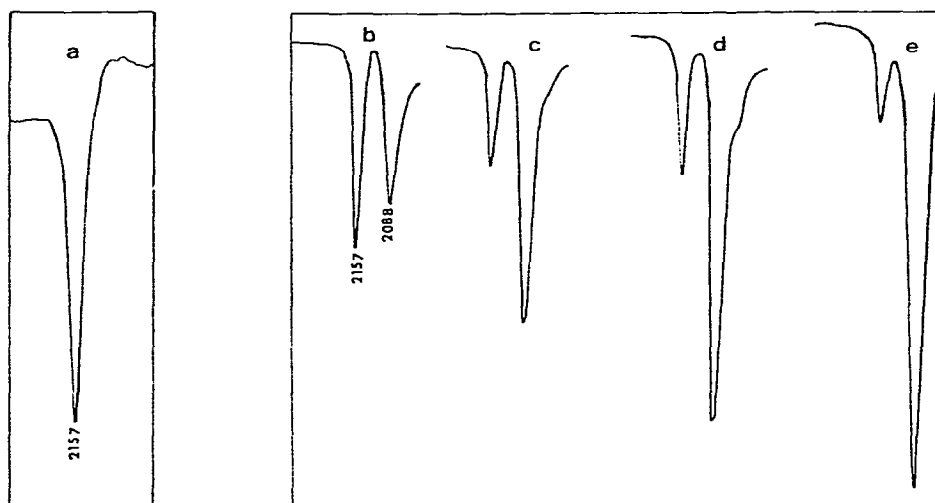
Fig. 5. IR spectrum of [Mn(p-CH$_3$OC$_6$H$_4$NC)$_6$] (PF$_6$)$_2$ in ν(C—N) region. a) CHCl$_3$ + HNO$_3$ solution; b) CHCl$_3$ solution, freshly prepared; c) after 5 min; d) after 10 min; e) after 15 min.

ascribed this anomalous behaviour in solution to dimer formation giving rise to spin-pairing.

Recently [7] it was emphasized that complexes of Mn^{II} with aromatic isocyanides undergo rapid reduction to Mn^{I} compounds in solution, and we believe that this is the reason for this apparently anomalous magnetic behaviour. In fact the addition of a few drops of nitric acid is sufficient to prevent reduction and to obtain paramagnetic solutions. The ESR spectra of the Mn^{II}

TABLE 5

ELECTRON POPULATIONS FOR RNC MOLECULES

| R	Atom/AO	s	p_x	p_y	p_z	Charge
C_2H_5	1	1.677	0.695	0.669	1.089	−0.130
	2	1.261	1.308	1.324	1.112	−0.005
	3	0.893	1.032	0.968	0.903	0.113
	4	1.024	1.021	0.990	0.988	−0.023
	5, 6	0.999				0.001
	7, 8, 9	0.988				0.012
C_2H_3	1	1.677	0.688	0.649	1.091	−0.105
	2	1.252	1.310	1.311	1.119	0.008
	3	1.030	1.001	0.987	0.891	0.091
	4	1.075	0.984	1.053	0.971	−0.082
	5	0.978				−0.022
	6	0.970				0.030
	7	0.964				0.036
C_6H_5	1	1.677	0.698	0.653	1.093	−0.120
	2	1.264	1.305	1.306	1.128	−0.005
	3	1.057	0.989	0.986	0.879	0.089
	4, 8	1.013	0.974	1.034	1.012	−0.033
	5, 7	1.015	0.999	0.969	1.012	0.005
	6	1.073	0.959	1.050	0.969	−0.050
	9, 13	0.963				0.038
	10,12	0.969				0.031
	11	0.997				0.003
p-$CH_3C_6H_5$	1	1.675	0.691	0.665	1.092	−0.123
	2	1.272	1.311	1.305	1.125	−0.013
	3	1.056	0.980	1.042	0.868	0.053
	4, 8	1.016	0.980	1.005	1.016	−0.018
	5, 7	1.014	0.989	1.010	1.007	−0.019
	6	1.50	0.966	0.979	0.991	−0.018
	9	0.997	0.973	0.973	1.045	−0.014
	10, 13	0.963				0.037
	11, 12	0.968				0.032
	14, 15, 16	0.994				0.006
p-$CH_3OC_6H_5$	1	1.676	0.680	0.688	1.097	−0.159
	2	1.269	1.303	1.291	1.112	0.015
	3	1.041	0.9581	1.099	0.861	0.042
	4	1.018	0.993	0.971	1.016	0.003
	5	1.013	0.977	1.076	1.006	−0.072
	6	1.085	0.994	0.933	0.836	0.152
	7	1.010	0.972	1.072	1.007	−0.062
	8	1.018	0.994	0.973	1.014	0.002
	9	1.559	1.475	1.864	1.294	−0.192
	10	1.031	0.903	0.974	0.937	0.145
	11	0.962				0.038
	12	0.960				0.040
	13	0.958				0.042
	14	0.961				0.039
	15, 16, 17	1.014				−0.014

[a]The numbering of the atoms is given in Fig. 3.
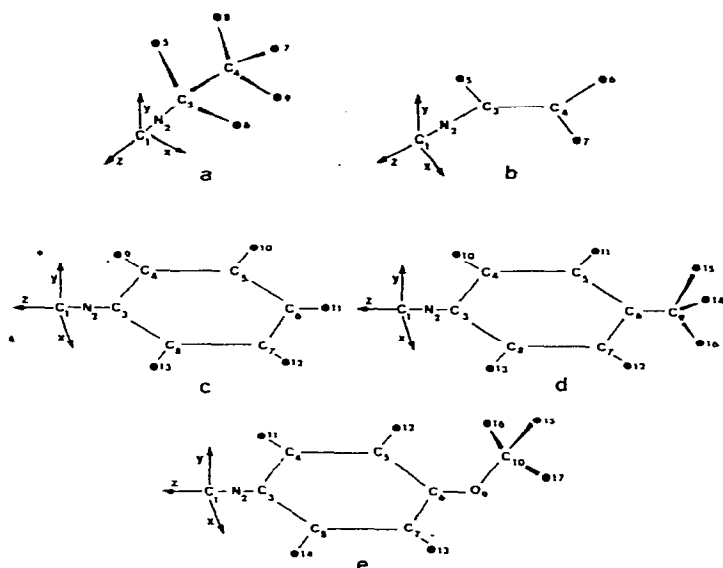
Fig. 3. Numbering of the atoms and local axes orientation for RNC molecules: a) C_2H_5NC; b) C_2H_3NC; c) C_6H_5NC; d) p-$CH_3C_6H_4NC$; e) p-$CH_3OC_6H_4NC$.

aliphatic isocyanide complexes in $CHCl_3$ or CH_3CN solution, and of those with aromatic isocyanides in the same solvents to which a few drops of nitric acid have been added both at room temperature and at $-160°$, show only six signals in which the g tensor values are all very close to 2 (see Table 6). It can thus be concluded that these compounds have a ligand field of O_h symmetry. The PMR spectra at room temperature, in CD_3CN in solution for the Mn^{II} complexes with the aliphatic isocyanide and in CD_3CN containing a few drops of nitric acid for the aromatic ones, show characteristic paramagnetic shifts for the resonance as compared with the corresponding Mn^I complexes spectra (see Fig. 4). These shifts reported in Table 7, must be essentially contact shifts since, as shown by the ESR spectra, $g_\parallel$ and $g_\perp$ are equal and so any pseudo-contact contribution must be negligible.

TABLE 6

EXPERIMENTAL ERS PARAMETERS

Compound	g Room temp.	$A \cdot 10^4 (cm^{-1})$	g $-160°$	$A \cdot 10^4 (cm^{-1})$	Solvent
$[Mn(CH_3NC)_6](PF_6)_2$	2.002	85.693	2.010	a	CH_3CN
$[Mn(C_2H_5NC)_6](PF_6)_2$	2.011	89.43			CH_3CN
	2.011	88.71	2.036	77.27	CH_3Cl
$[Mn(C_6H_{11}NC)_6](PF_6)_2$	2.005	85.61			CH_3CN
$[Mn(C_6H_5CH_2NC)_6](PF_6)_2$	2.019	87.99	2.018	87.95	CH_3CN
$[Mn(C_6H_5NC)_6](PF_6)_2$	2.016	87.89			$CH_3CN(HNO_3)$
$[Mn(p\text{-}CH_3C_6H_4NC)_6](PF_6)_2$	2.019	87.99	2.018	87.95	$CH_3CN(HNO_3)$
$[Mn(p\text{-}ClC_6H_4NC)_6](PF_6)_2$	2.012	86.40			$CH_3CN(HNO_3)$
$[Mn(p\text{-}CH_3OC_6H_4NC)_6](PF_6)_2$			2.008	84.39	$CHCl_3(HNO_3)$
	2.022	86.84	2.008	87.79	$CH_3CN(HNO_3)$

aSpectrum not well resolved.

TABLE 7. ISOTROPIC CONTACT SHIFT FOR [Mn(RCN)$_6$](PF$_6$)$_2$ COMPLEXES[a]

R		[Mn(RCN)$_6$](PF$_6$)	[Mn(RCN)$_6$](PF$_6$)$_2$	Contact shift
C$_6$H$_5$	o	−448	+ 132	+ 580
	m	−448	−712	−264
	p	−448	+ 140	+ 588
p-CH$_3$C$_6$H$_4$	o	−440	+ 268	+ 708
	m	−440	−687	−247
	CH$_3$	−143	−454	−311
p-CH$_3$OC$_6$H$_4$	o	−430	+ 193	+ 623
	m	−430	−575	−145
	CH$_3$	−228	−426	−132
C$_6$H$_5$CH$_2$	o	−433	−450	−17
	m	−433	−450	−17
	p	−433	−450	−17
	CH$_2$	−285	−130	+ 155
C$_2$H$_5$	CH$_2$	−220	b	
	CH$_3$	−84	−83	+ 1
CH$_3$		−190	−109	+ 81

[a] Data are from spectra in CD$_3$CN at 60 MHz relative TMS, and are measured in Hz to an accuracy of ± 1Hz.
[b] Undetectable signal, probably too broad (see ref. 28).

TABLE 8
CN STRETCHING FREQUENCIES (cm^{-1}) IN CHCl$_3$ OF THE Mn^I COMPLEXES (in CH$_2$CL$_2$ solution)

Compound	IR	Raman
[Mn(CH$_3$NC)$_6$]PF$_6$	2124[a]	2220 p[a]
		2155 dp
[Mn(C$_2$H$_5$NC)$_6$]I	2095	2195 p
		2132 dp
[Mn(C$_6$H$_{11}$NC)$_6$]Cl	2089	2200 p
		2120 dp
[Mn(C$_6$H$_5$CH$_2$NC)$_6$]ClO$_4$	2106	2210 p
		2135 dp
[Mn(C$_6$H$_5$NC)$_6$]PF$_6$	2085	2190 p
		2115 dp
[Mn(p-CH$_3$C$_6$H$_4$NC)$_6$]I	2086	2190 p
		2116 dp
[Mn(p-ClC$_6$H$_4$NC)$_6$]ClO$_4$	2085	2190 p
		2116 dp
[Mn(p-CH$_3$OC$_6$H$_4$NC)$_6$]NO$_3$	2088	2185 p
		2120 dp

[a] In CH$_2$Cl$_2$ solution.

TABLE 9. CN STRECTCHING FREQUENCiES (cm^{-1}) OF THE Mn^{II} COMPLEXES

Compound	Colour	IR	Raman
[Mn(CH$_3$NC)$_6$](PF$_6$)$_2$	Light pink	2220[a]	2260 p[b]
			2245 dp
[Mn(C$_2$H$_5$NC)$_6$](PF$_6$)$_2$	Light pink	2207[c]	2245 p[c]
			2225 dp
[Mn(C$_6$H$_{11}$NC)$_6$](PF$_6$)$_2$	Light pink	2190[c]	2230 p[c]
			2212 dp
[Mn(C$_6$H$_5$CH$_2$NC)$_6$](PF$_6$)$_2$	Orange	2203[c]	2245 p[c]
			2225 dp
[Mn(C$_6$H$_5$NC)$_6$](PF$_6$)$_2$	Red	2165[d]	e
[Mn(p-CH$_3$C$_6$H$_4$NC)$_6$](PF$_6$)$_2$	Blue	2162[d]	e
[Mn(p-ClC$_6$H$_4$NC)$_6$](PF$_6$)$_2$	Violet	2171[d]	e
[Mn(p-CH$_3$OC$_6$H$_4$NC)$_6$](PF$_6$)$_2$	Blue	2157[d]	e

[a] In CH$_3$CN solution. [b] In HNO$_3$ solution. [c] In CHCl$_3$ solution. [d] In CHCl$_3$ solution with addition of a few drops of nitric acid. [e] Decomposes because of absorption of the source radiation.

The spectra of the aromatic isocyanide complexes show an alternative in the sign of the contact shifts of the *ortho* and *meta* protons of the aromatic ring, characteristic of a system in which the spin density is predominantly distributed by spin polarization within the π orbitals, so that the unpaired electron of the manganese must occupy a π-type orbital, that is, in octahedral symmetry the ground state must be $^2T_{2g}$. This conclusion is confirmed by the fact that the aliphatic isocyanide complexes, which have a poorer capacity to act as π-delocalizating systems, give much smaller contact shifts (see Table 7).

In the region characteristic of C—N stretching the IR spectra of the Mn^I and Mn^{II} compounds, show only one band, both in the solid and in solution, whereas the Raman spectra, again in both states, show two bands at frequencies different from the IR band (see Table 8 and 9). These experimental facts are in accordance with group theory, which, for O_h symmetry predicts:

$$\Gamma_{\nu(C-N)} = A_{1g}(R) + E_g(R) + T_{1u}(IR)$$

The T_{1u} frequency, the only IR active one, is thus automatically assigned; the A_{1g} and E_g frequencies have been assigned from the solution Raman spectra where the A_{1g} band becomes polarized. In the solution spectra of the Mn^I compounds the A_{1g} band is less intense than the E_g band, whereas for the Mn^{II} complexes the opposite is true. This difference in behaviour is most probably connected with the oxidation state of the metal since analogous behaviour [29] has been reported for the compounds $K_5[Mn(CN)_6] \cdot H_2O$ and $K_4[Mn(CN)_6] \cdot 3H_2O$. The IR spectra of the Mn^{II} aromatic isocyanide complexes were obtained using chloroform solutions containing a few drops of nitric acid since in the absence of acid rapid reduction to Mn^I compounds occured, as can be seen in Fig. 5, where the time dependent IR spectrum of $Mn[(p\text{-}CH_3OC_6N_4NC)_6](PF_6)_2$ is shown. This figure shows that reduction from Mn^{II} to Mn^I does not occur with corresponding oxidation of the coordinated isocyanide, since in such cases there would be a decrease in the symmetry of the complex at least from O_h to C_{4v} and so the number of the bands in the C—N stretching region would increase to at least three. The reduction is also not accompanied by the dissociation of the complex since no bands were observed in the IR spectrum which could be attributed to free isocyanides. With respect to the Mn^I compounds the Mn^{II} complexes show increase in the C—N stretching mean frequency considered as:

$$\bar{\nu} = 1/6(3\nu_{T_{1u}} + 2\nu_{E_g} + \nu_{A_{1g}})$$

This behaviour seems to confirm that, as expected, in going from Mn^I to Mn^{II} there is a decrease in back donation.

The electronic spectra of the Mn^{II} complexes were recorded in $CHCl_3$ solution in the case of the aliphatic compounds and in $CHCl_3$ containing a little nitric acid in the case of the aromatic compounds. The value of Δ for the Mn^{II} isocyanide complexes should be ca. 33 kK, similar to the values calculated for the analogous Mn^I compounds [8] from the observed transitions at 31.25 and 37.00 kK. The d—d transitions in the spectra of the aliphatic Mn^{II} complexes appear as weak shoulders on the intense bands probably of the type $\pi_M^* \rightarrow \pi_L^*$

TABLE 10

$\pi_L^b \to \pi_M^\star$ ELECTRONIC TRANSITIONS OF [Mn(CNR)$_6$](PF$_6$)$_2$ COMPLEXES

| R	Energy (cm^{-1})	log ϵ
C$_2$H$_5$	28,570	2.98
C$_2$H$_3$	22,220^a	
C$_6$H$_5$	20,481	2.43
p-ClC$_6$H$_4$	19,084	3.34
p-CH$_3$C$_6$H$_4$	18,691	3.78
p-CH$_3$OC$_6$H$_4$	15,584	3.84

^{a}From ref. 28.

and are obscured in the case of the aromatic compounds by internal ligand charge-transfer bands.

In all the spectra a relatively intense energy band lower than 30 kK appears characterized by a strong red shift from ligand to ligand (see Table 10), which we tentatively assign to the C.T. $\pi_L^b \to \pi_M^\star$. Since under our experimental conditions the presence of Mn^I can be excluded, in contrast to Matteson and Bailey [29], we believe that the colour of the complexes is not due to a Mn$^I \rightleftharpoons$ Mn^{II} equilibrium but to the nature of the isocyanide.

Electronic spectra require more detailed discussion because, better than ESR and IR spectra, they show how much our calculations fit the experimental data.

Discussion on the electronic spectra of Mn^{II} complexes

Since a theoretical calculation of the $\pi_L^b \to \pi_M^\star$ transition in molecules containing many atoms is a very difficult task, we prefer to discuss the observed red-shift in a qualitative manner. According to Jørgensen [30] the charge transfer energy in a octahedral complex is given as the difference between the ionization potential [*IP*(L)] for:

$$\ldots (\pi_L^b)^2 (\pi_M^\star)^5 \to \ldots (\pi_L^b)(\pi_M^\star)^5$$
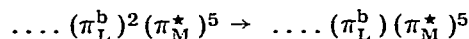
and the electronic affinity (*EA*(M)) for:

$$\ldots (\pi_L^b)^2 (\pi_M^\star)^5 \to \ldots (\pi_L^b)^2 (\pi_M^\star)^6$$
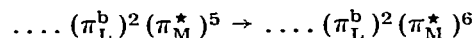
corrected for the contribution $-J$(M,L) which takes account of the attraction between the electrons in the $\pi_M^\star$ and the hole created in π_L^b. The charge-transfer energy is thus *IP*(L) — *EA*(M) — *J*(M,L)i.e. *IP*(L) — *IP*(M) + *J*(M,M) — *J*(M,L).

In the ligand series reported in the above tables, *IP*(L) decreases strongly (see Table 4); in the corresponding series of Mn^{II} complexes, *IP*(M) is expected to increase slightly because the lowering in energy of the FVMO of the ligand should produce a larger back-donation from the metal. Hence the 3d orbitals of type $\pi_M^\star$ should be stabilized and the *IP*(M) must increase. The values of *J*(M,M) may be however considered to be practically constant. The values of *J*(M,L) calculated using the CNDO and point charge approximations, expressed in eV are, for instance, 4.11 (ethyl isocyanide) 3.47 (vinyl isocyanide) and 3.14 (phenyl isocyanide). Qualitatively the red shift may thus be essentially determined by the variation in *IP*(L) along the series of ligands.

The charge transfer in question, on the hypothesis that it takes place to a molecular orbital which on the whole has $3d$ character, corresponds to a formal reduction of Mn^{II} to Mn^{I} and has an energy decreasing with the reducing power of the ligand.

This character of the ligand has already been correlated by us with the ionization potential, and has also been correlated with the "optical electronegativity" parameter χ_{opt} (L), defined [31] as:

$$\chi_{opt}(L) = 1/30 \, \sigma_{corr} + \chi_{opt}(M) = 1/30 \, [\sigma_{obs.} + D\{\langle S(S+1)\rangle - S(S+1)\}] + \chi_{opt.}(M)$$

where σ is the energy of the electronic transition in kK. Assuming that $\chi_{opt}(M) = 1.8$ and using a value of $D = 3.2$ kK, calculated according to Jørgensen [30] with $B(Mn^{++}) = 0.425$ kK [31], we obtain the following values for $\chi_{opt}(L)$: 2.6_8 (ethyl isocyanide), 2.4_7 (vinyl isocyanide), 2.4_1 (phenyl isocyanide), 2.3_6 (p-chloro phenyl isocyanide); 2.3_5 (p-tolyl isocyanide) and 2.2_5 (p-methoxyphenyl isocyanide). These values are all lower than the value of 2.8 for the CN^- anion, which is a strong reducing ligand.

The figure 2.8 may be obtained from the spectrum of $Mn(CN)_6^{4-}$ in which the $\pi_L^b \rightarrow \pi_M^*$ charge transfer has been found [31] at 31.25 kK.

Conclusions

This study points out some essential differences between the isocyanides. The electronic structure of the aliphatic terms is notably different from that of the aromatic ones, and calculations have shown that the isocyanide belonging to the first group are poorer π-acceptors, have higher ionization potentials and optical electronegativities than those belonging to the latter group. Octahedral complexes of the metal in the lower oxidation state should therefore be preferentially formed with the aromatic ligands, while the opposite should be true when the metal has a partly filled d shell, i.e. when charge transfer from the ligand to metal is possible. In such cases the instability of the complexes is mainly due to the low energy difference between the highest occupied MO of the ligand and the d orbitals of the metal. These conclusions seem to be in accordance with the result of polarographic oxidation studies of analogous Mn^{I} complexes [32]. Even is such a direct comparison of the spectroscopic and electrochemical results if not completely justified, it is interesting to note that the values of $E_{1/2}$ for the oxidation of the complexes follow an inverse course to that of our calculated $\chi_{opt}(L)$ values, so confirming in another way the scale of the reducing powers of the isocyanide. Any attempt to correlate in a simple manner the C—N stretching frequency and the π-acceptor ability of the ligand must be made with caution, since the shift in going from free ligand to complexed ligand is influenced by both kinetic and potential energy contributions. Preliminary calculations show that it is not easy to separate the two contributions, nor possible to transfer the kinetic contribution from one ligand to another; thus it is difficult to predict at which point the shift ceases to be linked to the back-donation mechanism. In order to solve this problem exactly,

TABLE 11

ANALYTICAL DATA FOUND (CALCD.) (%)

	C	H	N	M.P. (dec.) ($^{\circ}$C)
[Mn(CNCH$_3$)$_6$]PF$_6$ C$_{12}$H$_{18}$F$_6$MnN$_6$P	33.2 (32.3)	3.7 (4.0)	19.3 (18.8)	238
[Mn(CNCH$_3$)$_6$](PF$_6$)$_2$ C$_{12}$H$_{18}$F$_{12}$MnN$_6$P$_2$	23.9 (24.3)	3.0 (2.9)	14.2 (14.1)	245
[Mn(CNC$_6$H$_{11}$)$_6$]PF$_6$ C$_{42}$H$_{66}$F$_6$MnN$_6$P	59.3 (59.0)	7.2 (7.7)	9.9 (9.8)	153
[Mn(CNC$_6$H$_{11}$)$_6$](PF$_6$)$_2$ C$_{42}$H$_{66}$F$_{12}$MnN$_6$P$_2$	51.1 (50.4)	6.5 (6.6)	8.7 (8.4)	167
[Mn(CNCH$_2$C$_6$H$_5$)$_6$]PF$_6$ C$_{48}$H$_{42}$F$_6$MnN$_6$P	63.6 (63.8)	5.0 (4.6)	9.5 (9.3)	121
[Mn(CNCH$_2$C$_6$H$_5$)$_6$](PF$_6$)$_2$ C$_{48}$H$_{42}$F$_{12}$MnN$_6$P$_2$	55.5 (55.0)	4.0 (4.0)	8.1 (8.0)	128
[Mn(CNC$_6$H$_4$-p-Cl)$_6$]PF$_6$ C$_{42}$H$_{24}$Cl$_6$F$_6$MnN$_6$P	49.7 (49.2)	2.2 (2.3)	8.4 (8.2)	162
[Mn(CNC$_6$H$_4$-p-Cl)$_6$](PF$_6$)$_2$ C$_{42}$H$_{24}$Cl$_6$F$_{12}$MnN$_6$P$_2$	42.7 (43.1)	1.9 (2.0)	6.8 (7.1)	176

the geometries of both ligand and complex must be known, and a complete vibrational analysis performed to calculate the force constants. This will be the subject of future work.

Experimental

The ESR spectra were recorded with a Varian 4502-11 spectrometer in the X band with a field modulation of 100 kHz. The resonance frequencies were measured in an indirect mode on the frequency of the D.P.P.H. The PMR spectra were obtained using an NEVA NV 14 spectrometer operating at 60 M Hz with TMS as internal reference. The IR spectra were recorded on a Perkin - Elmer Model 621 spectrophotometer and the Raman spectra on a Coderg PHO apparatus with an Argon source. The electronic spectra were obtained using a Beckman DK 2A spectrophotometer.

Preparation of the compounds

The Mn^I derivatives were prepared according to the literature methods [33,35] and the Mn^{II} derivatives were prepared from the corresponding Mn^I compounds by oxidation by concentrated nitric acid in glacial acetic acid solution and subsequent addition of an aqueous solution of KPF$_6$ [28,34]. In Table 11 the analytical data are reported for the new compounds.

Acknowledgements

References

1 I. Ugi, Isonitrile Chemistry, Academic Press, New York, 1971.
2 L. Malatesta and F. Bonati, Isocyanide Complexes of Metals, John Wiley, New York, 1969.
3 J.M. Pratt and P.R. Silverman, J. Chem. Soc. A, (1967) 1286.
4 A. Sacco and F.A. Cotton, J. Amer. Chem. Soc., 84 (1962) 2043.
5 P. Boorman, P. Craig and T. Swaddle, Can. J. Chem., 48 (1970) 838.
6 Y. Dartiguenave, M. Dartiguenave and H.B. Gray, Bull. Soc. Chim. Fr., (1969) 4225.
7 V. Valenti, A. Sgamellotti, F. Cariati and L. Naldini, Ric. Sci., 38 (1968) 1230.
8 P. Fantucci, V. Valenti and F. Cariati, Inorg. Chim. Acta, 5 (1971) 3674.
9 A.C. Sarapu and R.F. Fenske, Inorg. Chem., 11 (1972) 3021.
10 F.A. Cotton, T.G. Dunne and J.S. Wood, Inorg. Chem., 4 (1965) 318.
11 G.V. van Dine and R. Hoffman, J. Amer. Chem. Soc., 90 (1968) 3227.
12 E. Clementi and D. Clint, J. Chem. Phys., 50 (1969) 4899.
13 T.K. Ha, J. Mol. Struct., 11 (1972) 185.
14 F. Millich, Chem. Rev., 72 (1972) 101.
15 D.S. Matteson and R.A. Bailey, J. Amer. Chem. Soc., 90 (1968) 3761.
16 J.A. Pople and D.L. Beveridge, Approximate Molecular Orbital Theory, McGraw-Hill, New York, 1970.
17 G.A. Segal: CNDO/2 - QCPE program n. 91.
18 C.C. Costain, J. Chem. Phys., 29 (1958) 864.
19 S.N. Gosh, R. Trambarulo and W. Gordy, J. Chem. Phys., 21 (1963) 308.
20 D.W. Turner, A.D. Baker and C.R. Brunde, Molecular Photoelectron Spectroscopy, J. Wiley, New York, 1970.
21 I. Langmnir, J. Amer. Chem. Soc., 41 (1919) 1543.
22 B. Back, L. Hansen-Nygaard and J. Restrup-Andersen, J. Mol. Spectrosc., 2 (1958) 54.
23 R. McWeeney, R. Mason and A.C.D. Towl, Discussions Faraday Soc., 1 (1969) 20.
24 F.A. Cotton, T.G. Dunne and J.S. Wood, Inorg. Chem., 3 (1964) 1495.
25 H.M. Powell and G.W.R. Bartindale, J. Chem. Soc., (1945) 799.
26 D.R. Armstrong, P.G. Perkins and J.J. Stewart, J. Chem. Soc. A, (1971) 3674.
27 G. Distefano, G. Innorta, S. Pignataro and A. Foffani, J. Organometal. Chem., 14 (1968) 165.
28 D.S. Matteson and R.A. Bailey, J. Amer. Chem. Soc., 89 (1967) 6389; J. Amer. Chem. Soc., 91 (1968) 1975.
29 W.P. Griffith and G.T. Turner, J. Chem. Soc. A, (1970) 858.
30 C.K. Jørgensen, Oxidation Numbers and Oxidation states, Springer-Verlag, Berlin, 1969; C.K. Jørgensen, Essay in Coordination Chemistry, Birkhäuser-Verlag, Basel, 1964.
31 J.J. Alexander and H.B. Gray, J. Amer. Chem. Soc., 90 (1968) 4260.
32 P.M. Triechel and G.E. Dirreen, J. Organometal. Chem., 39 (1972) C20.
33 A. Sacco and L. Naldini, Gazz. Chim. Ital., 86 (1956) 207.
34 L. Naldini, Gazz. Chim. Ital., 90 (1960) 871.
35 A. Sacco, Ann. Chim. (Rome), 48 (1958) 225.
36 R.G. Gillis and J.L. Occolowitz, J. Org. Chem., 28 (1963) 2924.
37 K. Bolton, N.L. Owen and J. Sheridan, Spectrochim. Acta, Part A, 25 (1969) 1.
38 K. Bolton, N.L. Owen and J. Sheridan, Spectrochim. Acta, Part A, 26 (1970) 909.
39 A.L.Mc Clellan, Tables of Experimental Dipole Moments, W.H. Freeman, London, 1963.