

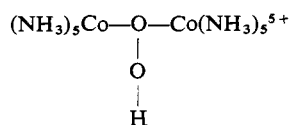
Table IV. Data for Cobalt(II)-Ammonia-O₂ System at 25°

$k_1^5 = 2.5 \times 10^4 M^{-1} \text{sec}^{-1}$	$k_{-2}^5 = 56 \text{sec}^{-1}$	$K_{O_2}^{5a} = 6.3 \times 10^6 M^{-2}$
$\Delta H_1^* = 4 \text{kcal mole}^{-1}$	$\Delta H_{-2}^* = 18 \text{kcal mole}^{-1}$	$\Delta H^a = 30 \text{kcal mole}^{-1}$
$\Delta S_1^* = -25 \text{eu}$	$\Delta S_{-2}^* = +9 \text{eu}$	

^aIn 15 M NH₃.

pared with that for cobalt(II) chelates in another paper.¹¹

Our observations on the reactivity of (NH₃)₅CoO₂Co(NH₃)₅⁴⁺ are consistent with two studies made of the reduction of (NH₃)₅CoO₂Co(NH₃)₅⁵⁺ in acid medium. Sykes¹³ observed the production of oxygen bubbles within a few seconds of completion of reduction by Fe²⁺, which can be ascribed to decomposition of the 4+ cation. Hoffman and Taube¹⁴ in reductions carried out with Cr²⁺, V²⁺, and Eu²⁺ detected a common intermediate which was assigned the structure



Its decomposition rate constant ($k = 5.0 \text{sec}^{-1}$ at 25° and

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[H⁺] = 1.0 M) is smaller than that observed by us for (NH₃)₅CoO₂Co(NH₃)₅⁴⁺ in alkaline solution, in agreement with the observation¹⁴ that the protonated form decomposes more slowly than the nonprotonated. It has been observed¹⁵ that the decomposition of (histidine-H)₂CoO₂Co(histidine-H)₂⁴⁺ is also retarded in strong acid due presumably to the formation of a more stable species, protonated at the bridge. The pK of this species was determined kinetically and spectrally as 1.2 ± 0.2 and is interestingly similar to that of the dibridged (en)₂Co(NH₂)(O₂H)Co(en)₂⁴⁺ (pK = 0.8).¹⁶

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The Charge-Transfer Spectra of Pyridine N-Oxide Metal Complexes. Determination of Optical Electronegativities

W. Byers,^{1a} B. Fa-Chun Chou,^{1b} A. B. P. Lever,^{1b} and R. V. Parish

Contribution from the Departments of Chemistry, University of Manchester Institute of Science and Technology, Manchester, England, and York University, Downsview, Ontario, Canada. Received September 20, 1968

Abstract: The metal-to-ligand charge-transfer spectra of octahedral Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) complexes of pyridine N-oxide and various methyl-, nitro-, and carboxyl-substituted derivatives are presented. The data are analyzed in terms of the concept of optical electronegativity. The charge-transfer bands are assigned as $t_{2g} \rightarrow \pi^*$ transitions in the complexes of Fe(II), Co(II), and Ni(II), and as $e_g \rightarrow \pi^*$ transitions in complexes of Mn(II) and Cu(II). A general method of assigning such spectra is discussed. The optical electronegativities of the octahedral Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) ions and the acceptor π^* orbitals of the ligand are calculated and discussed.

In one of the earliest studies of pyridine N-oxide metal complexes,² the unusual color, yellow, of the manganese(II) complex was pointed out and ascribed to the presence of a low-lying charge-transfer band. Since then there has been extensive activity in the investigation of pyridine N-oxide complexes,^{3,4} but no detailed discussion of the charge-transfer spectra of these complexes has appeared. Many pyridine N-oxide complexes exhibit a broad and

fairly intense band near 400 mμ which we attribute to a charge-transfer transition. In this paper, preliminary details of which appeared earlier,⁵ we present evidence supporting this contention and attempt to rationalize the variation of the band position with metal ion and ligand in terms of the concept of optical electronegativity.

Experimental Section

Electronic spectra were recorded with an Optika CF4NI double-beam grating spectrophotometer with a diffuse reflectance

(1) (a) University of Manchester Institute of Science and Technology; (b) York University.

(2) R. L. Carlin, *J. Amer. Chem. Soc.*, **83**, 3773 (1961).

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attachment. The compounds were prepared according to literature methods^{2,3,6} and analyzed satisfactorily.

Results and Discussion

The electronic spectra of octahedral first-row transition metal complexes of pyridine N-oxide may be conveniently divided into three regions: (i) 45,000–29,000 cm^{-1} , (ii) 29,000–21,000 cm^{-1} , and (iii) 21,000–5000 cm^{-1} .

Region i contains the π - π^* transition of the amine oxide ligand. This band is observed between 38,000 and 39,000 cm^{-1} in the Cr(III), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes of pyridine N-oxide (PyO) and 2- and 4-methylpyridine N-oxide (2- and 4-MePyO), which we have investigated (Table I). With 4-nitropyridine N-oxide (4-NO₂PyO), two bands are observed near 42,000 and 31,000 cm^{-1} . The latter band is associated with the nitro group. These data were obtained in the solid state. In acetonitrile solution, with the exception of the chromium(III) complex, the ultraviolet spectrum was identical with that of the free ligand. This is due to dissociation of the complexes in solution as previously pointed out by Drago.⁷ In the case of the chromium(III) complex, the kinetic stability of the d³ chromium ion precludes dissociation during the course of the measurement. An additional band was observed between 29,000 and 33,000 cm^{-1} in some of the complexes. It is a shoulder on the main absorption band near 38,000 cm^{-1} and is difficult to observe. Its assignment remains unknown. It is unlikely to be the n - π^* transition, which should be of high energy in the metal complex.

Table I. Diffuse Reflectance Spectra in the Ultraviolet Region

Compound	ν , cm^{-1}
PyO ^a	39,400 30,300 ^b
[Cr(PyO) ₆](ClO ₄) ₃	38,600
[Fe(PyO) ₆](ClO ₄) ₃	38,500 (29,150)
[Fe(PyO) ₆](ClO ₄) ₂	38,300
[Co(PyO) ₆](ClO ₄) ₂	38,300 (29,750)
[Cu(PyO) ₆](ClO ₄) ₂	38,900
[Zn(PyO) ₆](ClO ₄) ₂	38,500 (32,250)
[Ni(4-MePyO) ₆](ClO ₄) ₂	38,800 (31,250)
4-NO ₂ PyO	42,400
	30,500
[Fe(4-NO ₂ PyO) ₆](ClO ₄) ₂	43,700
	30,850
Ni(4-NO ₂ PyO) ₂ Br ₂	44,250
	31,000
[Cu(4-NO ₂ PyO) ₄](ClO ₄) ₂	42,400
	31,050

^a Solution spectrum: H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962. ^b n - π^* transition.

In region iii occur the crystal-field (d-d) bands which have been extensively discussed in the literature.³ Certain d-d bands are also located in region ii. It is region ii which is of special concern in this investigation. All the divalent ion complexes exhibit a strong band in this region, together with one or more shoulders on the low-energy

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tail (Table II). Since the ligands are transparent in this region, while, for most ions, the crystal-field transitions lie to lower energies, the bands in this region (ii) must be charge transfer in origin.

With a given ligand (PyO), the main band moves to higher energy in the sequence Mn(II) < Ni(II) = Fe(II) = Co(II) < Cu(II). Since the most difficult to oxidize species (Cu(II)) lies at highest energy, this infers⁸ that the charge transfer is from metal to ligand. The Fe(III) and Cr(III) complexes do not exhibit a peak in this region but do show shoulders on the rising absorption of the ultraviolet band. These shoulders are unassigned. The oxidizing nature of the ligand would suggest that this mode of electron transfer would occur at lower energy than the ligand-to-metal variety. This is confirmed by the observation that substituting an electron-withdrawing group, -NO₂, into the *para* position of the pyridine ring (4-NO₂PyO) moves the charge-transfer bands considerably to lower energy. In other words, by increasing the acceptor ability of the ligand, the energy of the charge-transfer band is decreased. Substitution of the electron-withdrawing CO₂ group in the *ortho* position (PicO) also leads to a decrease in the energy of the charge-transfer bands which now lie in the sequence⁹ Fe(II) < Co(II) < Ni(II) < Mn(II) < Cu(II). However, it does not follow that the assignment of the band is the same in all the complexes; in general this will not be the case.

Consider Figure 1 where the most probable assignments are indicated in a generalized form for a d⁸ system. The transition ν_2 will not necessarily have a lower energy than the transition ν_1 . If P is defined as the pairing energy,¹⁰ then

$$\nu_1 \cong \Delta E + 10Dq - P$$

$$\nu_2 \cong \Delta E$$

and

$$\nu_1 - \nu_2 \cong 10Dq - P \quad (1)$$

Since these complexes are magnetically high spin, then $10Dq < P$ by definition, and for the d⁸ system in question $\nu_1 < \nu_2$. In general, for these complexes ν_1 will occur at a lower energy than ν_2 (although they could lie close together) when there are one or more electron pairs in the t_{2g} set but no pairs in the e_g set. It follows that the lowest energy M → L charge-transfer band should be assigned in high-spin complexes as follows.



It is necessary to test this hypothesis with a theoretical model. Many approaches have been used^{8,11-14} to investigate and systematize charge-transfer spectra. We have chosen to rationalize our data using the optical

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Table II. Optical Electronegativity Data for Some Octahedral Amine Oxide Metal Complexes (Metal-to-Ligand Charge Transfer)

Metal	Compound	B , cm^{-1}	ΔSPE^a , cm^{-1}	Dq , cm^{-1}	CFSE^b , cm^{-1}	ν_{CT} , cm^{-1}	ν_{CT}^* , cm^{-1}	$\chi_{\text{opt}}(\text{L})$	$\chi_{\text{opt}}(\text{M})$
Mn(II)	Mn(PicO) ₂ · 2H ₂ O	835	15,590	850	-5100	24,700	14,220	0.8	1.3
Mn(II)	(Mn(PyO) ₆)(ClO ₄) ₂	835	15,590	850	-5100	24,330	13,840	0.8	1.3
						22,570 (sh)	12,080	0.8	1.2
Mn(II)	(Mn(4-MePyO) ₆)(ClO ₄) ₂	835	15,590	850	-5100	24,500	14,010	0.8	1.3
						22,300 (sh)	11,810	0.9	1.3
Mn(II)	(Mn(4-NO ₂ PyO) ₆)(ClO ₄) ₂	835	15,590	850	-5100	20,900	10,420	0.9	1.3
						19,310 (sh)	8,830	1.0	1.3
Mn(II)	Mn(PyO) ₂ Br ₂ ^c	835	15,590	850	-5100	26,320	15,830	0.7	1.2
						24,700 (sh)	14,210	0.7	1.2
Mn(II)	Mn(4-NO ₂ PyO) ₂ Cl ₂ ^c	835	15,590	850	-5100	21,800	11,310	0.9	1.3
						19,800 (sh)	9,310	0.9	1.2
Fe(II)	Fe(PicO) ₂ · 2H ₂ O	800	-14,930	1020	4080	21,000	31,850	0.8	1.9
Fe(II)	(Fe(PyO) ₆)(ClO ₄) ₂	800	-14,930	890	3560	25,250	36,620	0.8	2.0
						22,620 (sh)	33,990	0.85	1.95
Fe(II)	(Fe(4-MePyO) ₆)(ClO ₄) ₂	800	-14,930	860	3440	21,510	33,000	0.9	2.0
						19,610 (sh)	31,100	1.0	2.0
Co(II)	Co(PicO) ₂ · 2H ₂ O	770	-10,780	1030	4120	23,800	30,460	0.8	1.8
Co(II)	(Co(PyO) ₆)(ClO ₄) ₂	750	-10,500	910	3640	25,450	32,310	0.8	1.9
						22,900 (sh)	29,760	0.85	1.85
Co(II)	(Co(4-NO ₂ PyO) ₆)(ClO ₄) ₂	720	-10,080	870	3480	21,000	27,600	0.9	1.8
						19,800 (sh)	26,400	1.0	1.9
Co(II)	(Co(4-MePyO) ₆)(ClO ₄) ₂	760	-10,640	920	3680	25,200	32,160	0.8	1.9
						22,600 (sh)	29,560	0.9	1.9
Co(II)	Co(PyO) ₂ (NO ₃) ₂ ^c	750	-10,500	910	3640	27,700	34,560	0.7	1.9
Ni(II)	Ni(PicO) ₂ · 2H ₂ O	900	-8,400	935	3740	24,400	29,060	0.8	1.8
Ni(II)	(Ni(PyO) ₆)(ClO ₄) ₂	960	-8,960	810	3240	25,200	30,920	0.77	1.8
						22,800 (sh)	28,520	0.85	1.8
Ni(II)	(Ni(4-NO ₂ PyO) ₆)(ClO ₄) ₂	870	-8,120	800	3200	22,000	26,970	0.9	1.8
						19,800 (sh)	24,770	1.0	1.8
Ni(II)	(Ni(4-MePyO) ₆)(ClO ₄) ₂	960	-8,960	810	3240	24,900	30,620	0.8	1.8
						22,600 (sh)	28,320	0.9	1.8
Ni(II)	Ni(4-NO ₂ PyO) ₂ Br ₂	875	-8,170	690	2760	21,000	26,410	0.9	1.8
Cu(II)	Cu(PicO) ₂ · 2H ₂ O	1000	-4,670	1200	-7200	26,600	38,470	0.8	2.1
Cu(II)	(Cu(PyO) ₆)(ClO ₄) ₂	1000	-4,670	1250	-7500	27,400	39,570	0.8	2.1
Cu(II)	(Cu(PyO) ₄)(ClO ₄) ₂ ^d	1000	-4,670	1470	-8820	26,700	40,180	0.8	2.1
						22,950 (sh)	36,430	0.8	2.0
Cu(II)	(Cu(4-MePyO) ₄)(ClO ₄) ₂	1000	-4,670	1470	-8820	24,700	38,190	0.8	2.1
						22,600 (sh)	36,090	0.9	2.1
Cu(II)	(Cu(4-NO ₂ PyO) ₄)(ClO ₄) ₂ ^d	1000	-4,670	1470	-8820	21,300 (sh)	34,790	0.9	2.1
						19,300 (sh)	32,790	1.0	2.1

^a The ΔSPE values are as follows: Mn(II), $+8/3D$; Fe(II), $-8/3D$; Co(II), $-2D$; Cu(II), $-2/3D$; Ni(II), $-4/3D$. ^b The CFSE values are $+6Dq$ for Mn(II) and Cu(II), and $-4Dq$ for Fe(II), Co(II), and Ni(II). ^c Bridging amine oxide ligand. ^d Probably square.

electronegativity approach which was used most successfully by Jørgensen and coworkers⁸ in explaining the ligand-to-metal electron-transfer spectra of metal hexahalides (and tetrahalides¹⁵). This approach has not previously been used to elucidate metal-to-ligand charge-transfer spectra.

It assumes that the energy of a charge-transfer band is proportional, after correction for the change in spin-pairing energy during the transition, to the difference in electronegativity between the two orbitals involved. The "optical" electronegativity of a given orbital level is assumed to be a constant for a given metal ion or ligand in a given stereochemical environment. Jørgensen, in considering the optical electronegativity of a particular ion, refers in an octahedral complex to the approximately nonbonding t_{2g} level, and in a tetrahedral complex to the approximately nonbonding e level. Under such circumstances the optical electronegativity, $\chi_{\text{opt}}(\text{M})$ of a metal ion is expected to increase with increasing oxidation state. This is a particularly useful property since the Pauling electronegativity values do not take account of oxidation

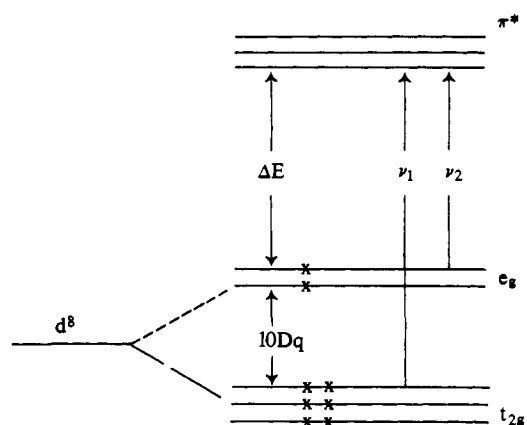


Figure 1. Schematic illustration of possible metal-to-ligand charge-transfer transitions in a d^8 metal complex.

state. We would also anticipate that the optical electronegativity would decrease with increasing coordination number since, in crystal-field theory, the spherical perturbation of the central ion orbitals is linearly dependent

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upon the number of ligands or point charges. Hence the χ_{opt} of Ni(II) in a tetrahedral environment should be higher than its value in an octahedral environment.

We shall not be concerned with the symmetry of the acceptor molecular orbital on the ligand atoms. It is probably an orbital triplet of odd symmetry, and transitions to it from either e_g or t_{2g} will be electronically allowed.

For metal (M) to ligand (L) charge-transfer spectra, the energy of the band, corrected for changes in spin-pairing energy, ν_{CT}^* , is given by

$$\nu_{\text{CT}}^* = 30,000(\chi_{\text{opt}}(\text{M}) - \chi_{\text{opt}}(\text{L})) \quad (2)$$

The constant 30,000 was introduced by Jørgensen⁸ so that the values derived would relate to the Pauling electronegativity scale. The spin-pairing energy (SPE) of a given configuration is given by

$$\text{SPE} = \{ \langle S(S+1) \rangle - S(S+1) \} D \quad (3)$$

where $\langle S(S+1) \rangle$ is the average value of $S(S+1)$ for a given configuration l^q and is given by

$$\langle S(S+1) \rangle = \frac{q(q+2)}{4} - \frac{(2l+2)q(q-1)}{2(4l+1)} \quad (4)$$

(l is the orbital quantum number, S is the total spin quantum number, and q is the number of electrons in the (in this case d) subshell).

D is called the *spin-pairing energy parameter* and, for d electrons, is approximately equal to $7B$ (B is the Racah parameter of interelectronic repulsion).⁸ SPE is not precisely the same as the previously defined¹⁰ pairing energy P .

For a nickel complex the charge-transfer transition may be represented by $t_{2g}^6 e_g^2 \rightarrow t_{2g}^5 e_g^2 \pi^*$. The ground state has $S = 1$, $q = 8$, hence $\text{SPE} = -2/3 D$. The excited state has $q = 7$, $S = 3/2$; hence $\text{SPE} = -2D$. Thus the change in spin-pairing energy is

$$\Delta \text{SPE} = -4/3 D$$

Values of ΔSPE may be similarly calculated for the other transition metal ions. The results are listed in Table II.

In order to relate the χ_{opt} values from one metal ion to another, the data will be referred to the spherically perturbed free ion. This procedure differs from that used by Jørgensen but seems more useful to us.

If the transition is from the t_{2g} level, then $4Dq$ is subtracted from ν_{CT} . If the transition is from the e level, $6Dq$ is added to ν_{CT} (see Figure 1) (ν_{CT} is the observed charge-transfer energy).

Then for transitions from t_{2g}

$$\nu_{\text{CT}}^* = \nu_{\text{CT}} - \Delta \text{SPE} - 4Dq \quad (5)$$

and for transitions from e_g

$$\nu_{\text{CT}}^* = \nu_{\text{CT}} - \Delta \text{SPE} + 6Dq \quad (6)$$

(Dq is the inseparable crystal-field parameter, not a product of the D and q quantities defined earlier). ΔSPE and Dq values may be evaluated by reference to the crystal-field (d-d) spectrum of the complex. Assuming an octahedral stereochemistry, the d-d bands of the Cr(III), Co(II), and Ni(II) complexes may be solved by standard methods^{13,16,17} to yield $B (=1/7 D)$ and Dq . In reality

these complexes are not octahedral,⁶ and transitions to the orbital triplets show some structure. However, for the present purpose it is a good approximation to treat them as octahedral. The mean positions of split bands were used to calculate Dq and B . Transitions to the first two maximum spin-orbital triplet levels were used to calculate Dq and B in the case of Cr(III) and Ni(II). It is incorrect to use the band near $25,000 \text{ cm}^{-1}$ as the third spin-allowed transition in the nickel complexes, as has been construed in the past;⁷ this is a charge-transfer band which undoubtedly masks the true position of the ${}^3T_{1g}(\text{P}) \leftarrow {}^3A_{2g}$ transition. The first and third spin-allowed transitions were used for the cobalt(II) complexes.¹⁸ For the manganese and iron derivatives it was not possible to obtain enough information from the spectra to calculate B . Hence in these cases values from the literature for the hexahydrates were used.¹⁶ In the case of copper a value of 80% of the free ion value of B was arbitrarily taken. For mixed ligand complexes the average $10Dq$ was employed.

From Dq , B , and ν_{CT} , values of ν_{CT}^* were obtained as indicated in Table II. These data allow the calculation of $\Delta \chi_{\text{opt}}$ ($\chi_{\text{opt}}(\text{M}) - \chi_{\text{opt}}(\text{L})$), but without having at least one reference value of χ_{opt} , the individual values of $\chi_{\text{opt}}(\text{M})$ and $\chi_{\text{opt}}(\text{L})$ cannot be derived.

While earlier work⁸ has established the $\chi_{\text{opt}}(\text{M})$ values of many heavy second- and third-row transition metal ions in an octahedral environment, little information has appeared concerning the first-row transition metal elements. Some $\chi_{\text{opt}}(\text{M})$ values for the first-row elements in tetrahedral environments have been obtained¹⁵ since $L \rightarrow M$ transitions in tetrahedral tetrahalides are more accessible than the corresponding octahedral bands. More recently Schmidtke¹⁹ has studied the charge-transfer spectra of a series of metal thiocyanates and selenocyanates in tetrahedral and octahedral complexes. The data on the MX_4^{2-} systems may be correlated with those of $\text{M}(\text{NCS})_4^{2-}$ and $\text{M}(\text{NCS})_6^{4-}$ (and the corresponding selenocyanate species) to generate $\chi_{\text{opt}}(\text{M})$ values for some octahedral first-row transition metal ions (if $\chi_{\text{opt}}(\text{M})$ and $\chi_{\text{opt}}(\text{L})$ are assumed to be transferable constants as is generally the case). Table III lists the necessary data used to calculate ν_{CT}^* from ν_{CT} in the $\text{Co}(\text{NCS})_4^{2-}$ and $\text{Co}(\text{NCS})_6^{4-}$ ions. Assuming $\chi_{\text{opt}}(\text{Co}(\text{II}), \text{T}_d) = 1.9$, values of $\chi_{\text{opt}}(\text{NCS}) = 2.7$ and $\chi_{\text{opt}}(\text{NCS}_e) = 2.6$ are obtained. These values may be inserted into eq 2 for some octahedral pseudohalides to yield (Table III)

$$\chi_{\text{opt}}(\text{Ni}(\text{II}), \text{O}_h) = 1.8$$

$$\chi_{\text{opt}}(\text{Co}(\text{II}), \text{O}_h) = 1.8$$

Either of these values may be utilized as a reference to generate individual $\chi_{\text{opt}}(\text{M})$ and $\chi_{\text{opt}}(\text{L})$ values for a series of amine oxide ligands. We chose to use the nickel complexes as standards. Values of the optical electronegativity of the bridging ligands were also generated although in practice these differed little from the terminal ligand values. Using the main absorption bands, the ligand electronegativity values are

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Table III. Optical Electronegativity Data for Some Pseudohalide Complexes (Ligand-to-Metal Charge Transfer)

Metal	Compound	Geometry	D (7B), cm ⁻¹	Δ SPE, ^a cm ⁻¹	Dq , cm ⁻¹	CFSE, ^b cm ⁻¹	ν_{CT} , cm ⁻¹	ν_{CT}^* , cm ⁻¹	$\chi_{opt}(M)$	$\chi_{opt}(L)$
Co(II)	Co(NCS) ₄ ²⁻	T _d	4800	+6400	450	+1800	31,000	22,800	1.9 ^c	2.7
Co(II)	Co(NCSe) ₄ ²⁻	T _d	4800	+6400	450	+1800	28,300	20,100	1.9 ^c	2.6
Co(II)	Co(NCSe) ₆ ⁴⁻	O _h	6000	+8000	970	-3880	29,400	25,280	1.8	2.6
Ni(II)	Ni(NCSe) ₆ ⁴⁻	O _h	6500	4330	1000	+6000	34,800	24,470	1.8	2.6
Ni(II)	Ni(NCS) ₆ ⁴⁻	O _h	6500	4330	960	+5760	38,000	27,910	1.8	2.7

^a The Δ SPE values are $+4/3D$ for Co(II) and $+2/3D$ for Ni(II). ^b The CFSE values are $+4Dq$ for Co(II) T_d, $-4Dq$ for Co(II), O_h, and $+6Dq$ for Ni(II), O_h. ^c Assumed.¹⁵

$\chi_{opt}(\text{pyridine N-oxide})$	= 0.8 (bridging, 0.7)
$\chi_{opt}(\text{4-methylpyridine N-oxide})$	= 0.8
$\chi_{opt}(\text{4-nitropyridine N-oxide})$	= 0.9
$\chi_{opt}(\text{2-picolinic acid N-oxide})$	= 0.8

The low-energy shoulder which appeared in many of the spectra was treated as a separate transition although its actual assignment remains unknown. Structure on charge-transfer bands may arise through intermediate coupling when the spin-orbit coupling coefficient of the coordinating ligand atom is large.⁸ Since oxygen is a light atom, structure from this mechanism is not anticipated. Since it is likely that the acceptor (π^*) orbitals on the ligand are degenerate, the excited configurations will contain several terms rather than one. The energies of these terms will differ because of varying interelectronic repulsion contributions. In general, we do not see composite charge-transfer bands arising from this situation, partly because some transitions will be forbidden and partly because, presumably, the variation in the interelectronic repulsion contribution is small. The presence of a main peak and a shoulder in most of our spectra may represent transitions to two different terms of the same excited configuration. The optical electronegativity values found for the ligands refer to unoccupied, presumably π^* molecular orbitals and are, of course, very much lower than those found for filled orbitals of ligands involved in ligand-to-metal charge transfer. These values are the first reported examples of the optical electronegativities of ligand acceptor orbitals. They may be introduced into the data for the other ions to derive $\chi_{opt}(M)$ values as shown in Table II.

The mean values obtained are

$$\chi_{opt}(\text{Mn(II), O}_h) = 1.3$$

$$\chi_{opt}(\text{Fe(II), O}_h) = 1.95$$

$$\chi_{opt}(\text{Co(II), O}_h) = 1.85$$

$$\chi_{opt}(\text{Cu(II), O}_h) = 2.1$$

Reference to Table II reveals that the data are, internally, highly consistent with the $\chi_{opt}(M)$ values for a given ion being essentially constant over the various ligands studied. This provides confidence that the procedure is meaningful.

The observed values of $\chi_{opt}(M)$, are, for the most part, compatible with the previously existing literature. The octahedral χ_{opt} values for cobalt(II), nickel(II), and copper(II) are slightly lower than for the tetrahedral species as anticipated. $\chi_{opt}(\text{Mn(II)})$ seems of the right order of magnitude in view of the size of the manganese(II)

atom. The value for iron(II) (2.0) seems rather high, in that the ease of oxidation of the iron(II) atom in many ferrous complexes would suggest a comparatively low electronegativity. While there is good agreement between Schmidtke's values¹⁹ for $\chi_{opt}(M)$ derived from the M(NCSe)_6^{4-} and M(NCS)_6^{4-} ions with $M = \text{Co(II)}$, Ni(II) , and Cu(II) , the agreement with Fe(II) is poor. Schmidtke cites $\chi_{opt}(\text{Fe(II)}) = 1.7$ after correction for the slightly differing definition of $\chi_{opt}(M)$. From our studies with other ferrous complexes, it seems possible that $\chi_{opt}(\text{Fe(II)})$ may be somewhat variable. The ease of oxidation may arise through the accessibility of the trivalent state rather than a low electronegativity. The deduction that the charge-transfer bands observed in the Mn(II) and Cu(II) compounds be assigned to $e_g \rightarrow \pi^*$ and those observed in Fe(II), Co(II) and Ni(II) be assigned to $t_{2g} \rightarrow \pi^*$ seems confirmed by our calculations. If the opposite assignments are employed, maintaining $\chi_{opt}(\text{Ni(II)}) = 1.8$, a value of $\chi_{opt}(L) = 1.2$ is derived. This value seems very high for an unoccupied π -antibonding ligand molecular orbital. Although it is true that there is no suitable reference with which to compare it, the lower value (0.8) seems more acceptable to us. Thus the initially proposed assignments find corroboration.

Despite the naïveté of the correction for the change in the interelectronic repulsion energy involved in these transitions, it does seem possible to deduce optical electronegativities from metal-to-ligand charge-transfer transitions. The comparative insensitivity of the $\chi_{opt}(L)$ values upon bridging of the ligand or upon substitution of the ligand is rather disappointing. However, it is not too surprising when one realizes that a change of 3000 cm^{-1} in the energy of an orbital corresponds to only a change of 0.1 electronegativity unit. This approach should prove useful in determining the relative energies of metal and ligand orbitals in a complex and identifying the orbitals involved in a transition. It is also a convenient and simple method of determining the electronegativities of ions in various stereochemistries.

Systematic studies of metal complexes exhibiting both crystal-field and charge-transfer spectra can provide some highly useful information about the effect of the metal-ligand bond on the energies of both the metal and ligand orbitals. In such a way the molecular orbital energy levels may be mapped.

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