

Single Crystal Polarized Electronic Spectra of a Five-Coordinate Macrocylic Complex of Nickel(II)

D. GATTESCHI and A. SCOZZAFAVA

Istituto di Chimica Generale dell' Università di Firenze and Laboratorio C. N. R.,
39 via J. Nardi, Florence, Italy

Received July 12, 1976

The single crystal polarized electronic spectra of the square pyramidal five coordinate complex $Ni(TMC)(N_3)ClO_4$, where TMC is the saturated macrocyclic ligand 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, have been recorded in the range of temperatures 4–300 K. The observed bands have been assigned to the $d-d$ transitions and guesses of the values of the ligand field parameters in the additive scheme have been made. It is suggested that the Dq value of the equatorial nitrogen donors is comparable to that of the corresponding non-cyclic amine complexes, and that it is mainly affected by the nickel–nitrogen distance.

Introduction

The interpretation of the electronic spectra of the complexes of transition metal ions with macrocyclic ligands is still controversial [1, 2]. In particular in many instances very high values of Dq have been attributed to the macrocyclic ligands [3]; although such values can be reasonable for unsaturated ligands, where π bonding effects become of paramount importance, they appear to us suspect in the case of saturated macrocyclic ligands, where the Dq value should be in our opinion mainly determined by the metal–nitrogen distance and therefore quite close to that of the corresponding non-cyclic amine complexes. Therefore single crystal spectroscopic studies are needed in order to determine exactly the Dq values. Structural data are not very abundant and in particular, only of few nickel complexes, which are well suited for spectroscopic studies, the X-ray structures have been reported, and among them $Ni(cyclam)Cl_2$ [4] (cyclam is 1,4,8,11-tetraazacyclotetradecane) and $Ni(TMC)(N_3)ClO_4$ [5] (TMC is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane). For the former complex we have suggested a value of Dq corresponding to that of other nickel amine complexes [6], on the basis of the reported diffuse reflectance spectra and of the nickel–nitrogen distance of the X-ray determination. However, single crystal data have been used to attribute a significantly higher value of Dq to such a ligand [7]. We intend to report

now the single crystal electronic spectra of the five coordinate square pyramidal $Ni(TMC)(N_3)ClO_4$ complex with the aim to substantiate our view on the Dq value for saturated macrocyclic ligands.

Experimental

Crystal Data

The X-ray crystal structure of $Ni(TMC)(N_3)ClO_4$ [5] has been determined to be orthorhombic, space group $Pnma$, with $a = 14.298$, $b = 9.641$, $c = 14.765$ Å, $Z = 4$. The site symmetry of the nickel atom is C_s , with the nickel–nitrogen in-plane distances of 2.10 Å. The Ni–Azide distance is 1.95 Å, the angle Ni–N–N being 135° . The crystals were kindly supplied by Prof. K. Barefield. They were plates with the (101) face most highly developed. It was possible also to cut some crystals along planes parallel to the (010) face.

Spectral Measurements

The room and liquid nitrogen polarized electronic spectra were recorded with the apparatus previously described [8]. Some spectra were run also on a Cary 17 spectrophotometer, and the liquid helium temperature spectra were run with a cryostat purchased from Oxford Instrument.

Polarized spectra were recorded both on the (101) and (010) faces, with the electric vector of the incident radiation parallel to the extinction directions a , b , c , and r (normal to b on the (101) face). In Figure 1 is reported a sketch of the chromophore.

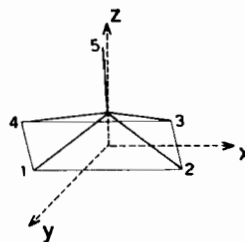


Figure 1. A diagrammatic sketch of the $[Ni(TMC)(N_3)]^+$ cation with the chosen molecular axes.

The x and y axes lie in the plane of the equatorial nitrogen donors, x lying also on the C_s site symmetry plane. The z axis is perpendicular to the plane of the four equatorial donors, making an angle of $\sim 5^\circ$ with the nickel-axial nitrogen direction. In Table I are reported the squares of the components of such axes along the a , b , c , and r directions.

TABLE I. The Squares of the Projections of the Molecular Axes along the Extinction Directions.

	a	b	c	r
x	0.89	0.00	0.11	0.50
y	0.00	1.00	0.00	0.00
z	0.11	0.00	0.89	0.50

Results

Description of the Spectra

The single crystal polarized spectra of the title compound show many bands, some of them neatly polarized. The band at about 6 kcm^{-1} is very intense in the spectrum recorded parallel to c (z) and far less intense along a (x) (see Figure 2). The ratio of the intensities is about 1:8. A small shift of the maxima (from 5.8 to 6.0 kcm^{-1}) is also observed. In the

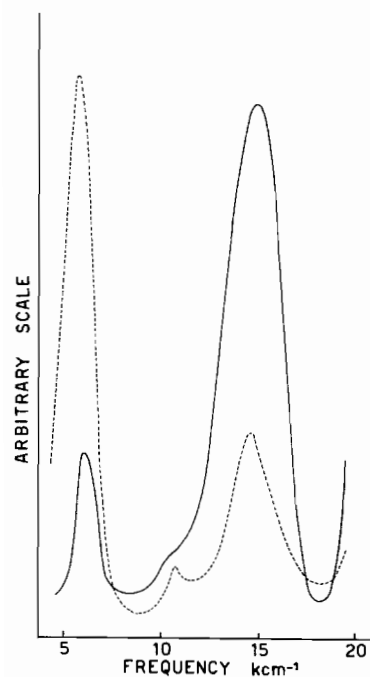


Figure 2. Single crystal polarized electronic spectra of $\text{Ni(TMC)(N}_3\text{)ClO}_4$ recorded on the (010) face at room temperature. (---) electric vector parallel to c , (—) electric vector parallel to a .

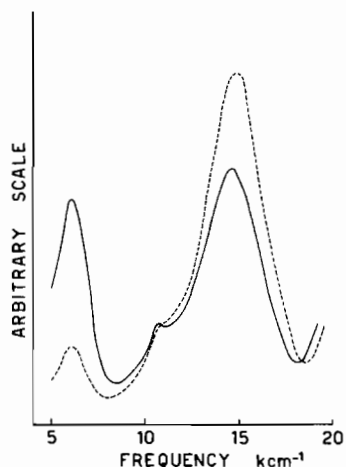


Figure 3. Single crystal polarized electronic spectra of $\text{Ni(TMC)(N}_3\text{)ClO}_4$ recorded on the (101) face at room temperature. (---) electric vector parallel to b , (—) electric vector parallel to r .

spectra recorded on the (101) face (Figure 3) the band is practically absent parallel to b (y) while it has intensity along r . It seems that the band is substantially z polarized, its intensity not varying appreciably down to liquid helium temperature.

In the region $10\text{--}13 \text{ kcm}^{-1}$ low intensity bands are observed. At room temperature a band at 10.8 kcm^{-1}

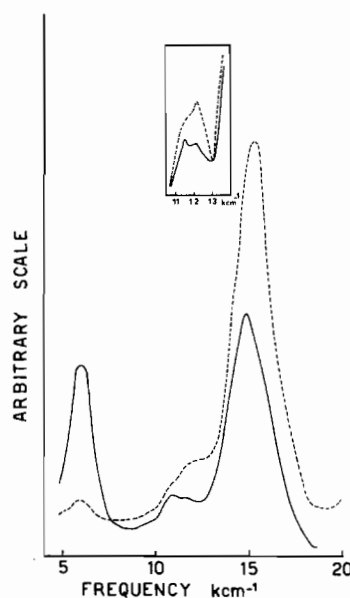


Figure 4. Single crystal polarized electronic spectra of $\text{Ni(TMC)(N}_3\text{)ClO}_4$ recorded on the (101) face at liquid nitrogen temperature. (---) electric vector parallel to b , (—) electric vector parallel to r .

Upper part of the bands in the range $11\text{--}13 \text{ kcm}^{-1}$, recorded on the face (010) at 4.2 K . (---) electric vector parallel to a , (—) electric vector parallel to c .

is clearly evident in the *c* and *r* spectra. At liquid nitrogen temperature the *r* and *b* spectra on the (101) face show two bands at 10.8 and 11.8 cm^{-1} (Figure 4) with no marked polarization properties. Finally at liquid helium temperature, in the spectra recorded on the (010) face, two maxima are observed at 11.5 and 12.2 cm^{-1} , the latter being more intense than the former in the spectrum parallel to *a* (Figure 4).

The band at 15 cm^{-1} is very intense parallel to *a* and far less intense parallel to *c*, the ratio of the intensities being $\sim 1:6$. On the (101) face the band is more intense parallel to *b*. There is a small shift of the maximum from 14.6 cm^{-1} in the *c* and *b* spectra to 14.9 cm^{-1} in the *a* and *r* spectra. It seems feasible that the band is allowed parallel to *x* and *y*.

The high frequency region is characterized by very intense absorptions, probably due to the proximity of electron transfer bands. The spectrum parallel to *c* shows a maximum at 24.5 cm^{-1} with the high frequency tail of the band slowly decreasing in intensity, and a shoulder at 26.8 cm^{-1} (Figure 5). In

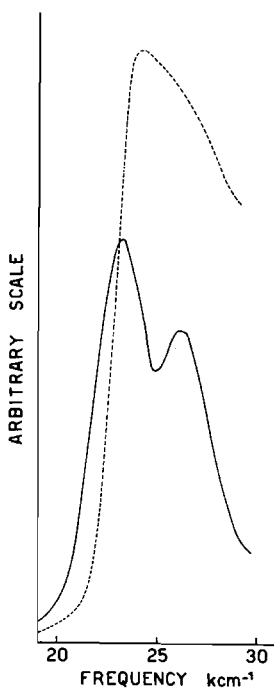


Figure 5. Single crystal polarized electronic spectra of Ni(TMC)(N₃)ClO₄ recorded on the (010) face at room temperature. (---) electric vector parallel to *c*, (—) electric vector parallel to *a*.

the spectrum parallel to *a* two maxima are observed at 23.4 and 26.2 cm^{-1} , the latter being less intense. The only change induced in the spectra by cooling to liquid helium temperature is a blue shift of the bands of about 6–700 cm^{-1} . The spectra parallel to *b* show a maximum at 26.1 and a shoulder at 23.7 cm^{-1} .

Finally the spectrum parallel to *r* shows a maximum at 25.6 cm^{-1} and a shoulder at 23.7 cm^{-1} . Also in this case the shape of the absorption band is similar to that of the *c* spectrum (Figure 6). These data seem to indicate that the bands at 26.2 and 23.4 cm^{-1} are *x* and *y* allowed, whereas the band at 24.5 cm^{-1} is *z* allowed.

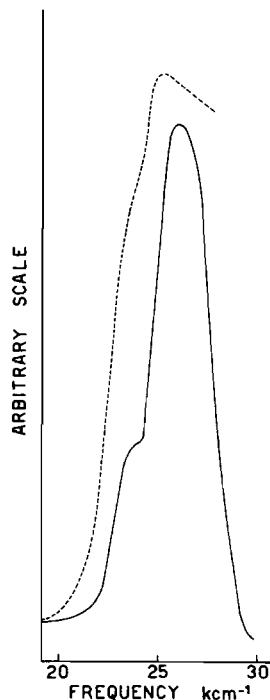


Figure 6. Single crystal polarized electronic spectra of Ni(TMC)(N₃)ClO₄ recorded on the (101) face at room temperature. (---) electric vector parallel to *r*, (—) electric vector parallel to *b*.

Assignment of the Spectra

In order to propose an assignment of the bands to the electronic transitions it is necessary to refer to an energy level diagram for a nickel(II) square pyramidal complex. Since in the present NiN₅ chromophore the four equatorial Ni–N distances are all equal, its overall symmetry is not far from C_{4v}, the main distortions being that the in-plane angles are 85° and 91° and that the nickel–azide bond makes a small angle to the normal to the plane of the other four nitrogen donors. In Figure 7 are reported the energy levels calculated in a ligand field scheme for a chromophore of C_{4v} symmetry. The variation of the parameters in the range expected for this complex shows that the ground state has to be ³B₁, a result which is in accord with previous reports by Gerloch [9]. Furthermore, the order of the excited levels corresponds to that previously reported, with the possible exception of the ³B₂ and ³A₂ levels.

On the basis of the energy level diagrams and of the similarity of the spectra to those reported by

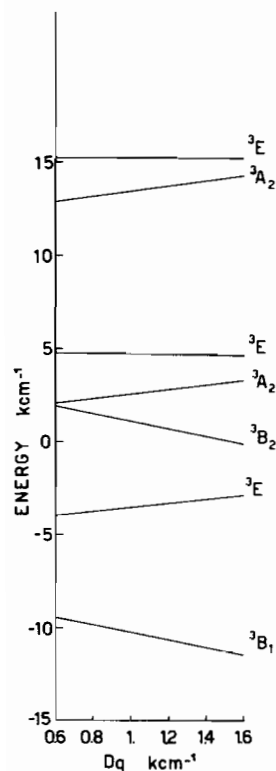


Figure 7. Energy level diagram for the triplet state of a five-coordinate square pyramidal (C_{4v} symmetry) nickel(II) complex, as a function of the Dq of the axial ligand. $Dq_{eq} = 1200 \text{ cm}^{-1}$; $(I_2/I_4)_{eq} = 0.55$; $\beta = 0.85$; $(I_2/I_4)_{N_3} = 0.50$.

Gerloch for the $[\text{Ni}(\text{MePh}_2\text{AsO})_4](\text{NO}_3)_2$ complex [9], in which the metal ion has C_{4v} symmetry, we assign the observed bands to the electronic transitions as recorded in Table II. In general we observe a blue shift of all the transitions of the present chromophore compared to those of NiO_5 , in accord with the higher field strength expected for the nitrogen donors. In particular the band at 10.8 cm^{-1} has been assigned to the transition ${}^3B_1 \longrightarrow {}^3B_2$, whose frequency depends only on the Dq value of the

equatorial macrocyclic ligand [10]. It can be considered as a support to the present assignment that a band quite close in energy to the present one is observed in the spectra of the corresponding halide derivatives of the macrocyclic complex [11]. In this framework, in fact, the constancy of the energy of the band can be considered as arising from the constancy of the nickel–nitrogen distance in the series of complexes, which in turn can be determined by the steric requirements of the ligand.

Comparing the polarization of the bands as they have been assigned by us with those predicted in C_{4v} symmetry, we see that for all the bands there is a good accord, except for the band at 5.9 cm^{-1} which in C_{4v} should be \perp polarized, while it is observed z polarized. Accurate checks were made of the dependence of the band intensity on temperature, but it was found to be practically constant from 4.2 to 300 K, making a vibronic mechanism unfeasible. Now the actual site symmetry of the nickel atom is C_s , the symmetry plane being xz . In this group it is required that the spectra in the y direction be different from those of the xz plane, while in the plane no definite prediction can be made, due to the fact that x and z span the same irreducible representation, but are not degenerate. By making the appropriate correlations, the selection rules of Table II can be derived. Obviously these are in accord with those of C_{4v} symmetry, except that they are looser, that is a band in C_s is in general allowed in more directions than in C_{4v} . In C_s therefore the band at 5.9 cm^{-1} is allowed also parallel to z and this makes the contrast between the assignment and the observed polarizations less dramatic. However it is not clear why the x and y components should be almost completely extinguished. We cannot offer a rationale for this fact, although we suspect that for this band spin–orbit coupling effects between levels lying close to the ground level may influence the selection rules of the symmetry group.

We have taken also into consideration the possibility that the effective symmetry is C_{2v} . In this

TABLE II. Observed and Calculated Transitions for the $\text{Ni}(\text{TMC})(\text{N}_3)\text{ClO}_4$ Complex.

C_{4v}	C_s	Frequency	
		Obsd.	Calcd. ^a
${}^3B_1 \longrightarrow {}^3E$ (1)	${}^3A'' \longrightarrow {}^3A'$ + ${}^3A''$ (x, y, z)	5.9 (z)	5.9
3B_2 (forbidden)	${}^3A'$ (y)	10.8 (low intensity)	11.3
3A_2 (forbidden)	${}^3A''$ (x, z)	11.8 (low intensity)	11.9
3E (1)	${}^3A'$ + ${}^3A''$ (x, y, z)	14.8 (x, y)	14.4
3E (1)	$\begin{cases} {}^3A'' \\ {}^3A' \end{cases}$ (x, z)	$\begin{cases} 23.4 \\ 26.2 \end{cases}$ (x, y)	25.0
3A_2 (forbidden)	${}^3A''$ (x, z)	24.5 (z)	22.8

^a $Dq_{eq} = 1200 \text{ cm}^{-1}$; $(I_2/I_4)_{eq} = 0.55$; $Dq_{N_3} = 700 \text{ cm}^{-1}$; $(I_2/I_4)_{N_3} = 0.50$; $\beta = 0.85$.

case the ground state should be 3A_2 and z polarized bands should arise from ${}^3A_2 \longrightarrow {}^3A_2$ transitions, and a possible assignment might be the following: ${}^3A_2 \longrightarrow {}^3A_2$ at 5.9 kcm^{-1} and 24.5 kcm^{-1} ; one of the two bands at $10\text{--}12 \text{ kcm}^{-1}$ is ${}^3A_2 \longrightarrow {}^3A_1$, the other being a spin forbidden transition; the other transitions are to 3B_1 and 3B_2 levels. Although this assignment cannot be discarded it seems to us unlikely, since it places the ${}^3A_2 \longrightarrow {}^3A_2$ transition lower than that observed in the NiO_5 chromophore [9]. In the following section we will show that fitting the transitions according to this assignment requires unreasonable values of the ligand field parameters.

Calculations

In order to substantiate the assignment, ligand field calculations were performed in C_{4v} symmetry, using the additive schemes [12] and the equivalence of Ligand Field and Angular Overlap parameters [13, 14]. For the $L_{ax}\text{--Ni--}L_{eq}$ angle the experimental value of 99° was used. For the equatorial sp^3 nitrogen donors, it was assumed that $I_2/I_4 = 0.55$ [14] which corresponds to $e'_\pi = 0$ and Dq varied in the range $1050\text{--}1350 \text{ cm}^{-1}$, while the parameters for the axial N_3^- ligand were let to vary in a larger range of values. The fit was checked by considering the relative square error sum. Satisfactory reproduction of the band maxima were obtained for the values $Dq_{N_3} = 600\text{--}800 \text{ cm}^{-1}$; $(I_2/I_4)_{N_3} = 0.2\text{--}1.0$; $Dq_N = 1150\text{--}1250 \text{ cm}^{-1}$. A typical fit is reported in Table II. The value of Dq for the macrocyclic ligand so obtained corresponds quite closely to the values reported for other nickel-amine nitrogen complexes [6]. According to the curve relating Dq and nickel-nitrogen distance [6] the value of Dq anticipated for the present complex is 1150 cm^{-1} , in very good agreement with the values calculated.

If on the other hand the transitions are assigned in C_{2v} symmetry (see previous section) the spectra can be fitted only by setting Dq_{N_3} negative which is clearly meaningless.

In our opinion therefore the present results show that the Dq values for saturated macrocyclic ligands are not significantly higher than those observed for non-cyclic amine ligands, and confirm that the main parameter determining the Dq value is the nickel-nitrogen distance.

Acknowledgments

Thanks are expressed to Prof. I. Bertini for helpful discussions and to Prof. L. Sacconi for encouragement. Prof. K. Barefield is gratefully thanked for providing crystals.

References

- 1 A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).
- 2 J. C. Dabrowiak, P. M. Merrell, and D. M. Bush, *Inorg. Chem.*, **11**, 1979 (1972).
- 3 D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **7**, 795 (1968).
- 4 B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Comm.*, 97 (1965).
- 5 M. J. D'Aniello, Jr., M. T. Mocella, F. Wagner, E. K. Barefield, and I. C. Paul, *J. Am. Chem. Soc.*, **97**, 192 (1975).
- 6 I. Bertini, D. Gatteschi, and A. Scozzafava, *Inorg. Chem.*, **15**, 203 (1976).
- 7 R. Sperati, *Ph. D. Thesis*, Ohio State University, 1971.
- 8 I. Bertini, D. Gatteschi, and F. Mani, *Inorg. Chem.*, **11**, 2454 (1972).
- 9 M. Gerloch, J. Kohl, J. Lewis, and W. Urland, *J. Chem. Soc. A*, 3269 (1972).
- 10 In the non-additive ligand field scheme the energy of this transition is $10 Dq$. The relation between Dq and Dq_{eq} for a five coordinate complex with $L_{ax}\text{--M--}L_{eq} = \theta$ is $Dq = \sin^4 \theta Dq_{eq}$.
- 11 E. K. Barefield and F. Wagner, *Inorg. Chem.*, **12**, 2435 (1973).
- 12 C. E. Schaffer, *Struct. Bonding (Berlin)*, **14**, 69 (1973).
- 13 M. Gerloch and R. C. Slade, "Ligand Field Parameters", Cambridge University Press, Cambridge, 1973.
- 14 I. Bertini, D. Gatteschi, and A. Scozzafava, *Inorg. Chem.*, **14**, 812 (1975).