Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332, U.S.A.

The Electronic Structure of Square-Planar Nickel(II) and Copper(II) Complexes

D. J. Royer, V. H. Schievelbein, A. R. Kalyanaraman, and J. A. Bertrand

Receveid August 13, 1971

The polarized single crystal spectra of $Ni(DACO)_2(ClO_4)_2\ 2H_2O$ *and* $Cu(DACO)_2 \cdot 2H_2O$ *indicate that the d orbital energy level order is* $d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$ *in both cases. The simple vibronic selection rules for* D_{4h} *symmetry apply quite well and simple ligand field calculations fit the observed spectra reasonably well. The crystal structure of* $Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$ *has been determined. It crystallizes in the triclinic space group* $P\bar{1}$ *with* $a = 8.586(6)$, $b = 9.324(2)$, $c = 16.863(4)$ Å, $\alpha = 156.34(2)^\circ$, $\beta = 86.80(2)^\circ$, $\gamma = 92.86^\circ$; $V = 540.95$ Å^3 *one formula unit per unit cell. The structure was solved and refined by conventional techniques, based on 525 reflections measured with a scintillation counter (Mo Kα radiation); the final R value was 0.087. The coordination of the nickel is strictly planar and square within experimental error. The x axis positions are effectively blocked with no coordination in that direction. Thus the metal is effectively exatly* D_{4h} *square planar.*

Introduction

The expected electronic structure for square planar $3d^n$ complexes of D_{4h} symmetry has been worked out theoretically rather completely some time ago, and can be found in a number of publications.[1] However, there has been very little direct experimental verification of the expected structure. Indeed the "d" orbital energy order $b_{1g}(d_{x^2-y^2}) > b_{2g}(d_{xy}) > e_g(d_{xz}, dd_{yz}) > a_{1g}(d_{z^2})$[2], which is the order usually predicted by ligand field calculations[3], has not been experimentally established for any $3d^n$ complex.

A large number of « square planar » $3d^n$ complexes have been studied by a variety of techniques, but they all seem to exhibit one or more of three different complicating factors which keep the results from being a true test of the ligand field predictions. These are: (1) extensive deviation of the coordination geometry from square; (2) extensive π bonding involving the e_g orbitals; and; (3) «residual» interactions along the *z* axis of the complex with anions or solvent molecules.

The acetylacetonate and other β-ketoenolate complex, and the salicylaldiminate complexes are examples that deviate so far from D_{4h} symmetry that their *effective* symmetry is usually no higher than D_{2h} which leads to several types of difficulty[4].

The presence of unsaturated and conjugated ligands give rise to π bonding with the metal which can lead to considerable shifts in the energy of the e_g orbitals. This shift, which can be to either higher or lower energy, could be taken into account in an MO approach to the problem, but it is rather complex.

Probably the most serious difficulty in most cases is the « residual » interaction along the *z* axis. There is considerable experimental exidence that the energy of the a_{1g} orbital is very sensitive to even quite weak interaction along the z axis.[5,6,7]

One ligand which seems to offer the possibilty of minimizing all of these difficulties and giving essentially simple planar coordination is 1,5-diazacyclooctane (DACO). The ligand is saturated, and so any difficulty with π bonding is eliminated. The ligand ring is flexible enough so that the square coordination should not be seriously distorted, and an inspection of models of the *bis*-DACO complexes of Cu^{II} and Ni^{II} indicated that the 3 and 7 methylene groups of the ligand should effectively sterically block any additional interactions along the *z* axis.

We have carried out an X-ray diffraction study of the crystalline $Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$. Our results show that while the ligands do not have the conformation that was expected, the coordination around the metal is square planar within experimental error, and the *z* axis positions are vacant and blocked by the ligand rings.

Single crystal polarized spectra of the nickel and copper complexes then enable us to identify the *d-d* transitions.

Experimental Section

Preparation. The 1,5-diazacyclooctane (DACO) was prepared by the method of Terent'ev, Kost, and Chursina[8] and by the method of Buhle, Moore, and

---

(1) For example G. Maki, *J. Chem. Phys.*, *28*, 651 (1958) gives a ligand field approach while H.B. Gray, *Trans. Metal Chem.*, *1*, 239 (1965) gives an MO approach.

(2) The usual orientation of the axes is used here with the ligands lying on the $x,y(b_{1u})$ axes.

(3) The order $b_{1g} > b_{2g} > a_{1g} > e_g$ has also been predicted. The order depends upon the relative sizes of the three ligand field parameters involved.

(4) M.A. Hitchmann and R.L. Belford, *Inorg. Chem.*, *10*, 984 (1971. and previous work cited therein.

(5) R.L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, *26*, (1957).

(6) D.J. Royer, *J. Inorg. Chem.*, *11*, 151 (1959).

(7) I.M. Procter, B.J. Hathaway, and P. Nickolls, *J. Chem. Soc.* (*A*), 1678 (1968).

Wiseloge.[9] Neither method gave particularly good yields and so the simpler procedure of Buhle *et al.* was used to prepare most of the material.

The *bis*(DACO)copper(II) perchlorate dihydrate and *bis*(DACO)nickel(II) perchlorate dihydrate were prepared by the procedure described by Musker and Hussain.[10] The infrared and visible spectra agreed with those reported by the previous workers.

Anal. Calcd for $Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$: Ni 11.3. Found 11.5. Clcd for $Cu(DACO)_2 \cdot 2H_2O$: Cu 12.1. Found 12.4.

Spectra. Single crystals of area of about 0.3 mm^2 and thickness of 0.05 to 0.1 mm were mounted on microscope slides and masked. The direction of polarization and the crystallographic axes were carefully noted using a polarizing microscope. The mounted crystal was adjusted in the sample beam of a Beckman DK-1 spectrophotometer, and a similarly masked microscope slide was placed in the reference beam. When polarized spectra were obtained, a sheet of Polaroid type NH38 was placed in both the sample beam and reference beam.

The crystals were grown from 90% ethanol solution. The nickel complexes were grown from bulk solutions and the copper complexes were grown between two microscope slides held apart by aluminum foil spacers.

The crystals were always mounted so that the light entered and left the crystal perpendicular to the crystal faces.

Collection and Reduction of the X-ray Data. The crystal for the space group determination was needle-shaped and of approximate dimensions $0.3 \times 0.7 \times 0.3$ mm, it was mounted along the long dimension (b^*-axis). Precession photographs, using Zr-filtered Mo Kα radiation (λ = 0.7107 Å), indicated a triclinic unit cell; P1 was asumed and the successful refinement of the structure has confirmed that assumption.

The crystal was transfered to an automated Picker four-circle diffractometer; 12 reflections were used to refine cell parameters by a least-squares procedure. The cell parameters obtained are a = 8.586(6) Å, b = 9.324(2) Å, c = 16.863(4) Å, α = 156.34(2)°, β = 86.20(2)°, γ = 92.86(2)°, and V = 540.95 $Å^3$ (25°, Mo Kα radiation). The calculated density of 1.60 g/cm^3 for one formula unit per unit cell agrees well with the observed density of 1.60(2) g/cm^3 measured by the flotation method using a benzene bromoform mixture.

The x-ray intensity measurements were made on the same crystal as used for the unit cell determination and Mo Kα radiation was again used. The intensities were measured with a scintillation counter mounted 21 cm from the crystal; the intensities were collected by the θ-2θ scan technique with a takeoff angle of 1.6° and a scan rate of 1° per min. A symmetrical scan of 2° was taken about the calculated position for each reflection; stationary beckground counts of 20 sec. were taken at the beginning (bgd1) and at the end(bgd2) of the scan. Calibrated copper attenuators were used in collection of data; the threshold point was set so that the counting rate would not exceed 10^4 counts/second. The pulse height analyser was set for approximately a 90% window, centered on the Mo Kα peak. A recorder monitored the scan of each peak and the scans were examined for erratic background and for the inclusion of Kβ peaks. A standard reflection (432) was intermittently scanned to check for instrument or crystal variations; no significant variation in the number of counts for this refection was observer during the entire data collection period. Corrected intensities (I) were obtained from the total integrated peak count (CT) acording to the equation

$$I = CT - 0.5(t_c/t_b)(bgdl + bgd2)$$

where t_c is the scan time and t_b is the counting time of each background (either bgdl or bgd2). The corrected intensities were assigned standard deviations acording to the equation

$$\sigma(I) = [CT + 0.25(t_c/t_b)^2(bgdl + bgd2)]^{1/2}$$

A total of 525 reflections were accepted as statistically above background on the basis that $\sigma(I)/I$ was less than 0.05. The intensities were corrected for Lorentz and polarization effects; since the linear absorption coefficient, μ, was 12 cm^{-1} it was not necessary to correct for absorption.

Solution of the Structure Computations were carried out on a Burroughs B-5500 computer and a Univac 1108 computer; programs employed included modified versions of F. L. Carter's program for calculating diffractometer settings, Zalkin's FORDAP Fourier summation program, the Busing-Martin-Levy XFLS and ORFFE least-squares and function and error programs, Johnson's ORTEP thermal ellipsoid plotting program, and various locally written programs. In structure factor calculations, the scattering factors tabulated by Ibers[11] were employed for all atoms.

With only one formula unit per unit cell in space group $P\bar{1}$, the nickel ion must occupy a position of $\bar{1}$ symmetry and was, thus, placed at the origin of the unit cell. Coordinates for the chlorine atoms were obtained from a three-dimensional Patterson synthesis and all remaining nonhydrogen atoms were located by successive structure factor and electron density calculations. Full-matrix least-squares refinement with individual isotopic temperature factors and with all refections weighted at unity converged to a conventional R value ($\Sigma || F_o | - | F_c || / \Sigma | F_o |$) of 0.147. The The oxygens of the perchlorate anion showed large thermal parameters and a difference Fourier showed residual electron density in the vicinity of the perchlorate ion. Anisotropic thermal parameters for nickel, chlorine, and the perchlorate oxygens were included in the least-squares refinement and the refinement converged to an R value of 0.087; a difference Fourier at this stage did not show any electron density above 0.7 e/$Å^3$. The final coordinates and thermal parameters are presented in Table I and the

---

(8) A.P. Terent'ev, A.N. Kost, and K.I. Churina, *Zhur. Obschchei Khin.*, *21*, 268.

(9) E.L. Buhle, A.M. Moore, and F.G. Wiseloge, *J. Am. Chem. Soc.*, *65*, 29 (1943).

(10) W.K. Musker and M.S. Hussain, *Inorg. Chem.*, *5*, 1417 (1966).

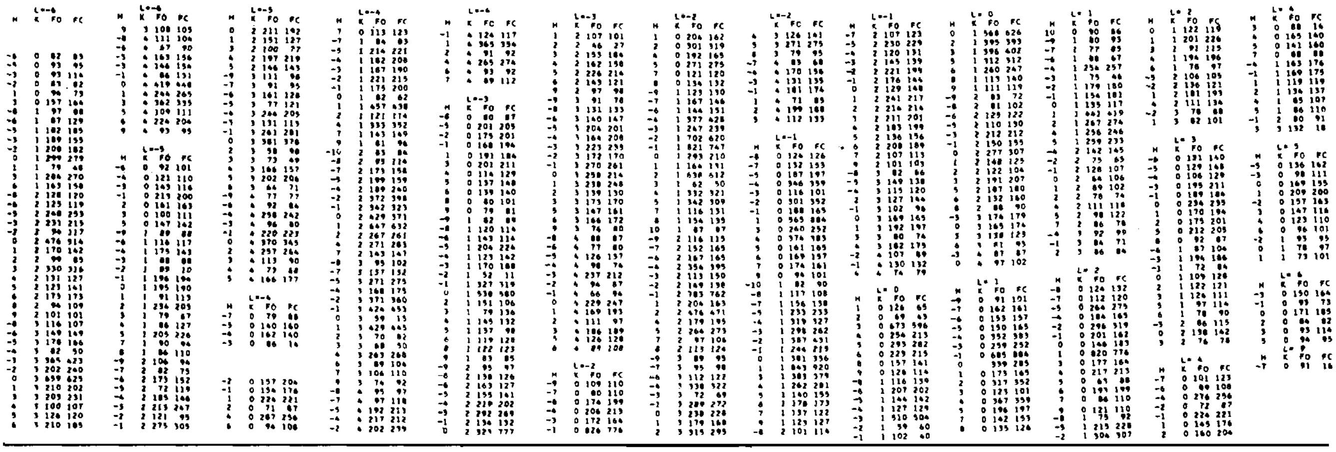
(11) J.A. Ibers in « International Tables for X-ray Crystallography », Vol 3, The Kynoch Press, Birmingham, England, 1962.

Table I. Final Positional and Thermal Parameters for $Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$

Atom	x	y	z	β_{11} or B^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0	0	0	0.0046(1)	0.0493(5)	0.0122(2)	−0.0010(1)	−0.0010(8)	0.0215(3)
N1	−0.012(2)[b]	0.133(6)	0.179(4)	4.6(7)					
N2	0.225(2)	−0.052(5)	−0.025(3)	4.4(7)					
C1	0.302(3)	0.285(7)	0.162(4)	7.8(13)					
C2	0.216(3)	0.524(8)	0.343(5)	9.4(15)					
C3	0.070(4)	0.480(8)	0.370(5)	7.8(13)					
C4	0.262(3)	−0.354(8)	−0.124(5)	7.8(13)					
C5	0.173(4)	−0.404(9)	0.069(6)	10.5(17)					
C6	0.032(4)	−0.179(9)	0.068(5)	7.2(12)					
Cl	0.357(1)	0.004(4)	0.346(2)	0.0189(2)	0.0855(11)	0.0328(4)	0.0064(4)	0.0080(3)	0.0484(6)
O1	0.319(8)	0.178(16)	0.482(7)	0.129(2)	0.233(6)	0.054(2)	−0.022(3)	0.014(2)	0.103(3)
O2	0.392(4)	0.246(9)	0.411(6)	0.074(1)	0.133(3)	0.056(1)	−0.026(1)	0.002(1)	0.075(2)
O3	0.454(4)	−0.230(9)	0.226(7)	0.049(1)	0.015(5)	0.173(2)	0.068(2)	0.045(1)	0.226(3)
O4	0.238(5)	−0.191(14)	0.249(9)	0.065(1)	0.504(9)	0.218(4)	−0.122(2)	−0.080(2)	0.325(6)
O5	0.350(2)	−0.008(4)	0.837(3)	5.4(7)					

[a] β_{11} for Ni, Cl, O1, O2, O3, and O4; B for other atoms. Anisotropic thermal parameters are expressed in the form: exp $-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)$. [b] Values in parentheses here and elsewhere in this paper indicate estimated standard deviations in the least significant digits.

Table II. Observed and Calculated Structure Factors (Electrons × 10) for $Ni(DACO)_2(ClO_4)_2 \cdot 2H_2O$.



final calculated structure factors and the observed values are listed in Table II.

Description of the Structure

The structure consists of $Ni(DACO)_2^{2+}$ cations, perchlorate anions, and water molecules; the waters and the perchlorate oxygens are too far from the nickel for cordination to be considered. A perspective view of the $Ni(DACO)_2^{2+}$ cations is shown in Figure 1; intramolecular distances and angles are presented in

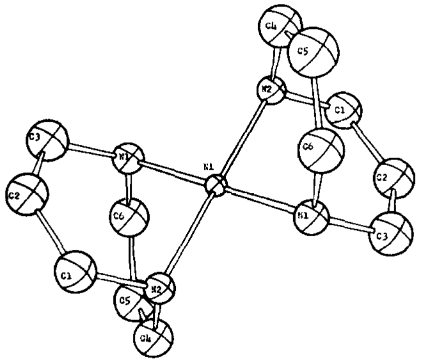


Figure 1. A perspective drawing of the cation, $Ni(DACO)_2^{2+}$.

Table III. Intramolecular Distances and Angles for $Ni(DACO)_2(ClO)_4)_2 \cdot 2H_2O$.

Intramolecular Distances, Å		Bond Angles, Deg.	
Atoms	Angle	Atoms	Distance
Ni-N1	1.95(3)	N1-Ni-N2	90.5(9)
N1-Ni-N2	1.94(2)	N1-Ni-N2′	89.5(9)
N2-C1	1.46(4)	Ni-N2-C1	112(1)
N2-C4	1.49(3)	Ni-N2-C4	109(1)
N1-C3	1.50(2)	Ni-N1-C3	112(2)
N1-C6	1.47(3)	Ni-N1-C6	108(2)
C1-C2	1.52(4)	C1-N2-C4	116(2)
C2-C3	1.47(4)	C3-N1-C6	117(3)
C4-C5	1.54(5)	N2-C1-C2	116(2)
C5-C6	1.51(4)	C1-C2-C3	132(1)
Cl-O1	1.08(4)	C2-C3-N1	114(2)
Cl-O2	1.34(4)	N2-C4-C5	121(2)
Cl-O3	1.21(2)	C4-C5-C6	121(3)
Cl-O4	1.25(2)	C5-C6-N1	122(3)
		O1-Cl-O2	101(4)
		O1-Cl-O3	129(6)
		O1-Cl-O4	97(4)
		O2-Cl-O3	110(3)
		O2-Cl-O4	124(3)
		O3-Cl-O4	98(3)

Table III. Since the nickel occupies a site of inversion symmetry and the only atoms within bonding distance are the four nitrogens of two diazacyclooctane molecules, the coordination of the nickel is exactly planar. Although the crystallographic site requires only C_i point symmetry for the cation, the two independent Ni–N distances {1,95(3) and 1.94(2)Å} are, within experimental error, equivalent and the symmetry of the cation is approximately D_{2h}; furthermore, the two independent N–Ni–N angles are, within experimental error, equal {90.5(9) and 89.5(9)°} and, if only the donor atoms are considered, the coordination symmetry is D_{4h}.

The coordination of the nickel to the two nitrogens of the eight-membered ring ligand creates two six-membered rings, both containing the nickel and two nitrogen atoms. A chair-boat conformation of the eight membered ring was predicted on the basis of molecular models and such a conformation would effectively block the fifth and sixth positions of an octahedron. However, the actual conformation of the eight-membered ring is best described as a planar eight-membered ring folded along the 1,5-axis (N,N axis). For each six-membered ring containing the nickel, five atoms (two N, three C) are essentially planar and only the nickel is bent out of the plane. The conformation is illustrated in Figure 2 in which the ligand is viewed along the N–N axis.

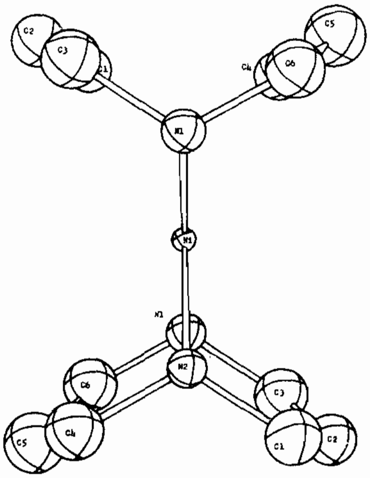


Figure 2. The Ni(DACO)$_2^{2+}$ cation as viewed along the N1-N2 axis.

Although the conformation is not that which had been predicted, the conclusion that octahedral coordination is prevented by steric factors may be valid since the protons on C2 and C5 afford some shielding of the axial positions. If normal bond angles, bond distances, and Van der Waals radii are assumed for the hydrogens on C2 and C5, two hydrogens are approximately 2.2Å apart directly over the axial positions. Neither the water molecules nor the perchlorate ions lie along these axial positions and closest extraionic contact along this axis is with one of the methylene chains of another cation.

Spectra

The aqueous solution spectrum of the *bis*(DACO) nickel(II) complex ion is shown in Figure 3, and the single crystal spectra of Ni(DACO)$_2$(ClO$_4$)$_2$ 2H$_2$O are shown in Figure 4. The single crystal spectra were taken with the crystal mounted so that the light beam was perpendicular to the crystal face parallel to the b^*, and c axes of the crystal. The « parallel » spectrum was taken with the electric vector approximately fourteen degrees from the b^* axis.[12] This orientation places the electric vector approximately five degrees from the z axis of the nickel complex. This slight misalignment should have very little effect on the spectrum.[13]

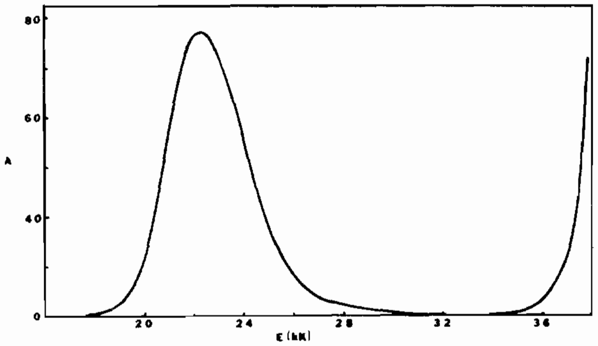


Figure 3. The spectrum of bis(1,5-diazacyclooctane)nicel(II) perchlorate in water.

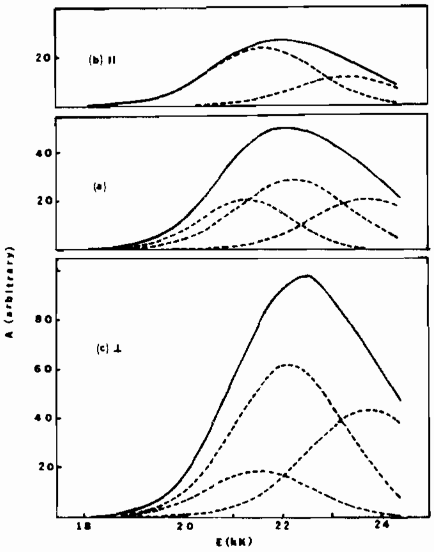


Figure 4. Single crystal spectra of Ni(DACO)$_2$(ClO$_4$)$_2$ · 2H$_2$O. (a) Nonpolarized; (b) Parallel to the z axis; (c) Perpendicular to the z axis.

The « perpendicular » spectrum was taken 90° from the parallel spectrum in the b^*, c plane.

The resolution of the observed spectra into Gaussian components was carried out using a locally written least squares computer program[14].

---

(12) The proper orientation could be found simply by rotating the polarizer until the position was found where the *d-d* peak at approximately 22kK showed minimum intensity.

(13) P.L. Meredith and R.A. Palmer, *Inorg. Chem.*, *10*, 1049 (1971).

(14) V.H. Schievelbein and D.J. Royer, presented at the Southeastern regional American Chemical Society Meeting, Atlanta, Ga. 1968.

Table IV. Gaussian Resolution of The d-d Spectra

		A[a]	E_{max}[b]	σ[c]	A	E_{max}	σ	A	E_{max}	σ	Error[d]
$Ni(DACO)_2^{2+}$	Solution	38.33	21.49	1.38	41.99	22.76	1.39	37.39	23.79	2.55	0.43
$Ni(DACO)_2(ClO_4)_4$ Crystal	Unpolarized	20.90	21.35	1.31	29.00	22.30	1.57	21.20	23.78	1.56	0.17
	Perpendicular	18.50	21.60	1.50	61.10	22.19	1.58	43.70	23.80	1.76	0.28
	Parallel	23.70	21.69	1.49	0.01	22.47	1.59	12.00	23.41	1.44	0.19
$Cu(DACO)_2^{+2}$	Solution	32.75	18.96	3.54	32.30	20.13	2.06	31.63	2074	3.53	0.14
$Cu(DACO)_2(ClO_4)_2$ Crystal	Unpolarized	16.92	18.23	2.96	32.81	20.96	1.98	21.40	23.13	2.36	0.28
	Perpendicular	54.95	18.16	2.56	32.82	20.78	2.07	52.03	23.05	2.13	0.81
	Parallel	2.91	19.75	2.04	32.35	20.83	2.14	5.78	23.49	1.85	0.19

[a] A = absorbance of the component band at its maximum: the solutions are in absorbancy units and the crystals are in arbitrary units. [b] E_{max} = The energy of the band maximum in kK. [c] σ = The conventional σ *i.e.* the half width at 0.417 A. [d] Error = The conventional standard error of fit.

Solution and crystal spectra of $Cu(DACO)_2(ClO_4)_2 \cdot 2H_2O$ were also obtained. The $Cu(DACO)_2(ClO_4)_2 \cdot 2H_2O$ crystals had an external shape quite similar to that of the nickel complex, but a check showed that the copper and nickel complexes are not isomorphous. However, the polarized crystal spectra of the copper complex can be resolved and then assigned in the same way as the nickel complex was if the *z* axis of the complex is assumed to be parallel to the long axis of the crystal.

The Gaussian resolution of the spectra of the copper and nickel complexes is summarized in Table IV. Two and four gaussian fits were also attempted and found to be unsatisfactory. The two gaussian fits sometimes gave errors of fit that were too large, and they also lead to large apparent shifts in the position of single components between different polarized spectra of the same species. The four gaussian resolutions did not lead to a reasonable fourth band. For example, a four gaussian resolution of the aqueous $Ni(DACO)_2^{2+}$ spectrum gave: $A_1 = 40.86$, $E_1 = 21.63$, $\sigma_1 = 1.44$; $A_2 = 37.02$, $E_2 = 22.87$, $\sigma_2 = 1.45$; $A_3 = 35.93$, $E_3 = 23.72$, $\sigma_3 = 2.70$; $A_4 = -0.51$, $E_4 = 26.57$, $\sigma_4 = 0.27$.

Discussion

The *d–d* spectra of the Nickel(II) and Copper(II) complexes both consist of single broad asymmetric peaks in the 20-22kK region which are well separated from the charge transfer bands which are located somewhere above 38kK. (This unusually great separation is another advantage of using a satuated ligand). The spectra could all be satisfactorily resolved into three gaussian components[15] as would be expected for complexes of D_{4h} symmetry. There is considerable evidence that such gaussian components can be considered to at least semiquantitatively represent the *d–d* single electron spin allowed spin allowed transitions[4-7,13,16-21].

The simple vibronic selection rules[22] for *d–d* transitions of nickel and copper complexes of D_{4h} symmetry can be worked out[23]. If we consider only the coordinated nitrogen atoms and the metal atoms, the odd vibrations are A_{2u}, B_{2u}, and $2E_u$, and the resultant vibronic selection rules for the one electron transitions from the $^1A_{1g}$ ground state of Ni(II) and the $^2B_{1g}$ ground state of Cu^{II} are given in Table V.

Table V. Vibronic Selection Rules For D_{4h} Symmetry. (The associated vibration is given in parenthesis)

	z	*x,y*
$A_{1g} \rightarrow A_{2g}$	Forbidden	Allowed (E_u)
$A_{1g} \rightarrow B_{1g}$	Allowed (B_{2u})	Allowed (E_u)
$A_{1g} \rightarrow E_g$	Allowed (E_u)	Allowed (E_u)
$B_{1g} \rightarrow B_{2g}$	Forbidden	Allowed (E_u)
$B_{1g} \rightarrow E_g$	Allowed (E_u)	Allowed (A_{2u},B_{2u})
$B_{1g} \rightarrow A_{1g}$	Allowed (B_{2u})	Allowed (A_{2u},B_{2u})

If we assume that all of the vibronic interactions are equally effective, the observed polarization of the transitions should be as given in Table V. On the other hand, both of the experimental spectra indicate that two of the three components show considerable polarization. Two different lines of argument have been advanced to explain polarization of bands of this type which should be vibronically allowed in all directions; (1) the argument that some vibrations should be more effective in promoting intensity than others[24,25], and (2) a consideration of the availability of low energy charge transfer states of the proper symmetry to mix with the excited "*d–d*" states.[4] In this case, both lines of argument support the same assignment.

An examination of Table V shows that the observed pattern of polarization will result if the out of plane bending vibration, B_{2u} is less effective than the other modes of vibration. This would lead to the follow-

---

(15) The true components are undoubtedly not true gaussians, but the fit to three gaussians in all cases gave fits where the error of fit of the calculated spectra to the experimental spectra was less than the experimental error of the experimental spectra.
(16) A.A.G. Tomlinson and B.J. Hathaway, *J. Chem. Soc.*, (*A*), 1685 (1968).
(17) R. Dingle, *J. Chem. Phys.*, *50*, 545 (1969).
(18) R. Dingle, P.J. McCarthy, and C.J. Ballhausen, *J. Chem. Phys.*, *50*, 1957 (1969).
(19) E.M. Holt, S.L. Holt, and K.J. Watson, *J. Amer. Chem. Soc.*, *92*, 2721 (1970).
(20) B.J. Hathaway, R.J. Dudley, and R.J. Fereday, *J. Chem. Soc.*, *A*, 571 (1970).
(21) L. Dubicki, M.A. Hitchman, and P. Day, *Inorg. Chem.*, *9*, 188 (1970).
(22) C.J. Ballhausen, « Introduction to Ligand Field Theory », McGraw-Hill, New York, N.Y. 1962 Chapt. 8.
(23) F.A. Cotton, « Chemical Applications of Group Theory, » Interscience, New York, N.Y. 1963.
(24) A.D. Liehr, *Advances in Chem. Phys.*, *5*, 241.
(25) R.L. Belford and J.W. Carmichael, *J. Chem. Phys.*, *46*, 4515 (1967).

ing predicted polarizations: for the nickel complex, the ${}^1A_{1g}\rightarrow{}^1E_{2g}$ should be essentially nonpolarized, the ${}^1A_{1g}\rightarrow{}^1B_{1g}$ transition should be largely polarized in the perpendicular direction, and the ${}^1A_{1g}\rightarrow{}^1A_{2g}$ should be essentially totally polarized in the perpendicular direction. The analogous polarizations for the copper complex are; ${}^2B_{1g}\rightarrow{}^2E_g$ nonpolarized, ${}^2B_{1g}\rightarrow{}^2A_{1g}$ mostly in the perpendicular direction, and ${}^1B_{1g}\rightarrow{}^2B_{2g}$ essentially totally in the perpendicular direction.

The symmetry of the excited *d-d* states are given in Table VI. If the accessable charge transfer states are considered to involve the *d, s,* and *p* orbitals of the metals and the "unshared" σ orbitals of the coordinated nitrogens only, the "charge transfer" states of ungerade symmetry accessable by one electron transitions from the ground state are ${}^1B_{2u}$ and ${}^1E_u$ for the nickel complex and ${}^2A_{2u}$ and ${}^2E_u$ for the copper complex. Therefore there should be no low lying charge stransfer states which can mix with the $A_{1g}\rightarrow B_{1g}$ and $B_{1g}\rightarrow A_{1g}$ transitions in the parallel direction, and thus these transitions will be unable to "borrow" much intensity from allowed transitions in this direction. Thus these two transitions should have low intensity in the parallel direction which leads to the same polarization predictions as the vibrational argument.

Table VI. Symmetry of the Allowed Vibronic Excited States.

Transition	z	x,y
$A_{1g}\rightarrow A_{2g}$	—	E_u
$A_{1g}\rightarrow B_{1g}$	A_{2u}	E_u
$A_{1g}\rightarrow E_g$		E_u
$B_{1g}\rightarrow B_{2g}$	$A_{1u},A_{2u},B_{1u},B_{2u}$	E_u
$B_{1g}\rightarrow E_g$	$A_{1u},A_{2u},B_{1u},B_{2u}$	E_u
$B_{gt}\rightarrow A_{1g}$	B_{2u}	E_u

The copper assignment is supported by the behavior of the high energy band when the complex is dis-$(DACO)_2(ClO_4)_2{\cdot}2H_2O$

${}^1A_{1g}\rightarrow{}^1E_g$	21.6kK
${}^1A_{1g}\rightarrow{}^1A_{2g}$	22.3kK
${}^1A_{1g}\rightarrow{}^1B_{1g}$	23.7kK

and for $Cu(DACO)_2(ClO_4)_2{\cdot}2H_2O$.

${}^2B_{1g}\rightarrow{}^2B_{2g}$	18.2kK
${}^2B_{1g}\rightarrow{}^2E_g$	20.8kK
${}^2B_{1g}\rightarrow{}^2A_{1g}$	23.1kK

The copper assignment is supported by the behavior of the high energy band when the complex is dissolved in water. The high energy band shifts much more when the ion is solvated than any of the other bands as would be eexpected for the transition involving the d_{z^2} orbital.[26]

In addition, simple crystal field arguments indicate that the ${}^1B_{1g}\rightarrow{}^1B_{2g}$ transition should be of lower energy than the ${}^1B_{1g}\rightarrow{}^1E_g$ transition. Thus all of our evidence supports the order $b_{1g}>b_{2g}>e_g>a_{1g}$ *for the d orbitals* in the copper complex. This assignment leads to the following values for the ligand field parameters for the copper complex; 10Dq = 18,2kK. Ds = 3.77kK, and Dt = 1.74kK.

A relatively simple ligand field calculation can be made which tends to confirm the assignment of the components of the spectrum of the nickel complex. An *a priori* ligand field calculation would clearly be of little use because we would have more adjustable parameters than peaks.

However, if we make some simplifying assumptions we can at least show that the assignments are reasonable. If it is assumed that the orbital splitting order is the same in the nickel and the copper complexes so that the ligand field parameters for the nickel complex are directly proportional to those of the copper complex, ligand field calculations can be carried out using the experimentally observed copper parameters and two adjustable parameters. The adjustable parameters are then, the proportionality constant between the nickel and copper parameters, and the parameter, β, which describes the reduction of the electron-electron repulsion from the free ion value. The necessary matrix elements have been given by Maki. Energy level diagrams were calculated for the nickel complex with β values from 1.0 to 0.70 and for orbital splittings from 100% to 125% of the values found in the copper complex. Some results are given in Figure 5. The variation of the parameters within the specified limits was found to give rise to only relatively small changes in the energy level pattern.

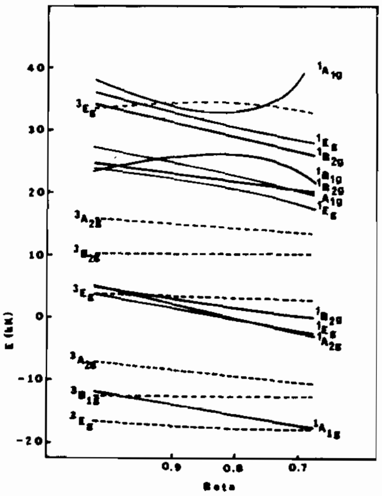


Figure 5. Energy levels calculated for $Ni(DACO)_2^{2+}$ as a function of β. The splitting of the *d* orbitals is taken as 125% of the splitting in $Cu(DACO)_2^{2+}$. (The energies are relative to the ${}^3F$ state of the free ion.

The three excited states arising by means of one electron "*d-d*" transitions from the ground state, ${}^1E_g$, ${}^1A_{2g}$, and ${}^1B_{1g}$, are always found quite close together and well separated from any other singlet states. Thus the calculation tends to confirm the contentions that all three of these terms are located in the single observed "*d-d*" band in the spectrum.

Probably the worst feature of these calculations is

---

(26) An examination of the relevant matrix elements[1] shows that the corresponding transition in the nickel spectrum, ${}^1B_{1g}\rightarrow{}^1A_{1g}$, should not be nearly as sensitive to perturbations along the z axis. The experimental spectra confirm this difference. The solution and crystal spectra of the nickel complex are virtually idential while the crystal and solution spectra of the copper complex are visibly different.

the obvious misplacement of the $^1A_{1g}$ ground term. This result is not unexpected because the introduction of β is not really sufficient to take into consideration the considerable amount of ligand character in the "$d_{x^2-y^2}$" orbital. However, the presence of relatively low lying triplet states is not unexpected, because the material shows a temperature independent paramagnetism of 0.54BM at 25°C.

Conclusions

The structural information, the spectral data, and the ligand field calculations all indicate that the nickel(II) and copper(II) DACO complexes are essentially simple square planar complexes free of the effects of π bonding and any additional interactions along the z axis, and that the simple ligand field predictions for such systems apply quite well. The observed d orbital energy order is $d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz} > d_{z^2}$ with a relatively large (>18 kK) separation between $d_{x^2-y^2}$ and d_{xy}, and with the remaining separations all considerably smaller (<6 kK). This is the arrangement that would be expected if there is considerable σ bonding interaction present to raise the energy of the $d_{x^2-y^2}$ orbital, and the order of the other orbitals is then determined by a relatively small purely electrostatic crystal field effect.

Acknowledgments. Funds from the Quality Improvement Program of the State of Georgia for the purchase of X-ray diffraction equipment are gratefully acknowledged; the help of the Rich Electronic Computer Center of Georgia Institute of Technology with computations is appreciated.