

radius for Tc(IV) from this structure. An upper limit would be 1.50 Å, based on the long bonds Tc(1)–Cl(2) and Tc(1)–Cl(3). The only other reported Tc–Cl bond length is 2.35 Å for the $\text{Tc}_2\text{Cl}_8^{3-}$ ion,¹⁵ in which the oxidation state of Tc is V or VI.

Acknowledgments.—We wish to thank Mrs. J. H. Hickford for supplying samples of the compound and

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The Crystal and Molecular Structure of Bis(2,2,6,6-tetramethylheptane-3,5-dionato)nickel(II)

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The crystal and molecular structures of bis(2,2,6,6-tetramethylheptane-3,5-dionato)nickel(II), also called bis(dipivaloylmethanido)nickel(II), $\text{Ni}(\text{DPM})_2$, have been determined in a single crystal X-ray diffraction study. The unit cell is monoclinic (space group $P2_1/a$) with dimensions $a = 10.70 \pm 0.01$ Å, $b = 10.98 \pm 0.02$ Å, $c = 10.39 \pm 0.02$ Å, $\beta = 113^\circ 16' \pm 15'$, and contains two formula units. As expected from earlier studies by Cotton and Fackler, the molecules are mononuclear, essentially planar, and centrosymmetric. The Ni–O distances, 1.836 ± 0.005 Å, are much shorter than those in a number of complexes in which Ni(II) is octahedrally coordinated by oxygen atoms. This may be explained by the absence of electrons in the antibonding σ -MO with d_{xy} symmetry. The orientation of the molecules in the unit cell is fully described for future reference in the reporting of polarized optical absorption studies of this substance and its isomorphous Cu(II) analog.

Introduction

Studies of β -ketoenolate complexes of nickel(II) and cobalt(II) have established that while the acetylacetonates readily form polymeric structures by sharing of oxygen atoms,^{1–5} the replacement of the methyl groups by larger groups leads to partial^{2,3} or complete^{2,3,6,7} dissociation, exclusively monomeric molecules being obtained when the methyl groups are replaced by the very bulky *t*-butyl group. Spectroscopic studies of the nickel² and cobalt^{4,6} monomeric complexes of 2,2,6,6-tetramethylheptane-3,5-dionato ion lead to the conclusion that these were, respectively, square and tetrahedral, and, for the cobalt complex, this has been conclusively demonstrated by single crystal X-ray diffraction study.^{6,7} The present paper reports an X-ray study which proves conclusively the planar structure of the nickel complex.

This study was undertaken not only to confirm this point but to provide knowledge of the orientation of the molecules in the unit cell for this compound and its isomorphous Cu(II) analog, in order that esr and

polarized electronic spectral studies of the crystals might be made. The results of the latter studies will be reported later. However, in anticipation, this paper will describe the molecular orientations more explicitly and in more detail than is customary in reports of crystal structure studies intended purely to elucidate molecular structures.

The ligand molecule, systematically named 2,2,6,6-tetramethylheptane-3,5-dione, has also the common name dipivaloylmethane, DPM, which has been often used in the past. Henceforth in this paper we shall use the latter name and its abbreviation.

Experimental Section

Bis(dipivaloylmethanido)nickel(II), $\text{Ni}(\text{DPM})_2$, was prepared by the reaction of dipivaloylmethane (2,2,6,6-tetramethylheptane-3,5-dione) and nickel acetate.⁸ The dipivaloylmethane was prepared by the method of Adams and Hauser.⁸ The product of the reaction of dipivaloylmethane with nickelous acetate was a green solid, believed to be the dihydrate of bis(dipivaloylmethanido)nickel(II). Upon drying under vacuum at 100°, the green solid lost water and turned red. The red solid was sublimed at 120° under a pressure of approximately 0.02 mm. A small amount of a yellow-green paperlike solid remained after sublimation. Sublimations were repeated until no residue was observed. Melting point determinations (uncorrected) on thrice sublimed material gave 224.5–225.5° in open-tube determinations and 225.0° in closed-tube determinations. Analysis of the thrice sublimed sample gave 62.32% carbon and 8.92% hydro-

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gen, which compares closely to the calculated values of 62.16 and 8.95%.

Platelike monoclinic prisms (crystal class $2/m$) were grown by sublimation under vacuum at 100° . Using a single crystal of about $0.5 \times 1.0 \times 0.1$ mm mounted on an axis in the plate, precession photographs were taken with Cu $K\alpha$ radiation. The unit cell was found to be monoclinic with a β angle of $113^\circ 16' \pm 15'$ and these dimensions: $a = 11.70 \pm 0.01$, $b = 10.98 \pm 0.02$, and $c = 10.39 \pm 0.02$ Å. The systematic absences observed were as follows: hkl no conditions; for $h0l$, $h \neq 2n$; for $0k0$, $k \neq 2n$. These conditions uniquely fix the space group⁹ as $P2_1/a$ (No. 14). The density (by flotation method in a saturated solution of KI at 30°) was found to be 1.15 ± 0.02 g/cm³. Taking the molecular weight as 424.7, the calculated number of molecules in the unit cell is 2.00 ± 0.08 .

Intensity data were recorded photographically by the equi-inclination Weissenberg method, using Cu $K\alpha$ radiation and multiple film technique. The $h0l$ through $h9l$ layers and the $hk0$ through $hk4$ layers were recorded and the intensities were estimated by comparison with a set of timed exposures of a reflection from the same crystal. No corrections were made for absorption due to the low value of the absorption coefficient ($\mu = 11.8$ cm⁻¹). It was calculated that 965 independent reflections would be available with Cu $K\alpha$ radiation in the range $0 < \sin \theta < 2^{-1/2}$, and measurements were restricted to that sphere in reciprocal space. Lorentz-polarization corrections by a graphical method¹⁰ were applied where required and necessary corrections for extension of spots on upper layer photographs¹¹ were made. It should be noted that of the approximately 965 reflections encompassed by the $h0l$ through $h9l$ layers, 248 were too weak to be recorded.

Determination of Structure

In the space group $P2_1/a$ the two nickel atoms occupy special positions $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0)$, which are inversion centers. The asymmetric unit consists of half of the nickel atom and one of the two chelate groups. It seemed likely that the position of the two oxygen atoms in the chelate ring could be obtained by a Patterson projection¹² onto the 010 plane by the overlap of nickel-oxygen vectors from the oxygen atoms in the chelate ring. The projection was made using 114 nonzero $h0l$ reflections. Two peaks lying 1.17 and 1.24 Å from the origin were located. Using the bond distances observed in the analogous zinc compound for the metal-oxygen bond length⁸ (Zn-O, 1.96 Å), trial positions for the two oxygen atoms were calculated.

Using the $h0l$ to $h9l$ set of reflections and the positions of the nickel atom and the two oxygen atoms, a structure factor calculation was made and a three-dimensional Fourier synthesis computed. The atomic scattering factors used were those of Freeman and Watson¹³ for nickel and those of Hoerni and Ibers¹⁴ for carbon and oxygen. The positions of the oxygen atoms were adjusted on the basis of this calculation. Three peaks were found representing the three carbon atoms in the ring. Another structure factor calculation and Fourier synthesis was made using the above atoms. Then the two carbon atoms representing the

centers of the *t*-butyl groups were located. From a further structure factor and Fourier calculation the positions of the six remaining carbon atoms were located. Three cycles of least-squares refinement¹⁵ in which the atom positions and the film scale factors were varied while fixed, arbitrary isotropic temperature factors were used lowered the unweighted residual from 0.36 to 0.27. The residual is defined as $\sum w ||F_o| - |F_c|| / \sum w |F_o|$, in which F_o and F_c are the observed and calculated structure factors and w is the weight, set equal to unity for all F_o values in calculating an "unweighted" residual. Three additional cycles of refinement in which scale factors, atomic parameters, and temperature factors were allowed to vary lowered the residual to 0.21.

At this point it became obvious that the large number of unobserved reflections was to be a problem. In order to reduce the number of unobserved reflections and to improve the data, the second set of reflections taken along the c axis, the $hk0$ through $hk4$ layers, was utilized. All reflections were corrected for Lorentz and polarization factors and spot extension and then put on the same relative scale by correlating intensities on the $hk0$ through $hk4$ films with those on the $h0l$ through $h9l$ films. The corrected intensities obtained on the $hk0$ through $hk4$ levels were averaged with the corresponding intensities observed on the $h0l$ through $h9l$ films. All unobserved reflections were assigned intensities of one-half the minimum value¹⁶ and were corrected for Lorentz and polarization factors and spot elongation in the same manner as the observed reflections. The number of nonobserved reflections was reduced from 248 to 201 after inclusion of the c axis data.

The reflections were now weighted. Those for which readings from both films were available were assigned a weight equal to the standard deviation σ_{F_o} of the average intensity (F_o). Using the theory of very small samples, the standard deviation was computed as being 0.89 of the difference between the two observed values.¹⁷ A plot of σ_{F_o} against F_o was made for all reflections with two observed values. It was assumed that those reflections for which only one value was available would follow the same relationship and σ_{F_o} was estimated from the plot for these reflections. For the unobserved reflections, which had been assigned an intensity of one-half the minimum observable (F_{\min}), a weight of $(1/\sqrt{12})F_{\min}$ was assigned on the basis of statistical considerations.¹⁷

A correction of the atomic scattering factors for nickel for the real part of the anomalous dispersion was made according to the method of Dauben and Templeton.¹⁸ The imaginary term was neglected.

Two cycles of isotropic refinement were run and small adjustments made to positional parameters on the basis of a three-dimensional Fourier synthesis. Two fur-

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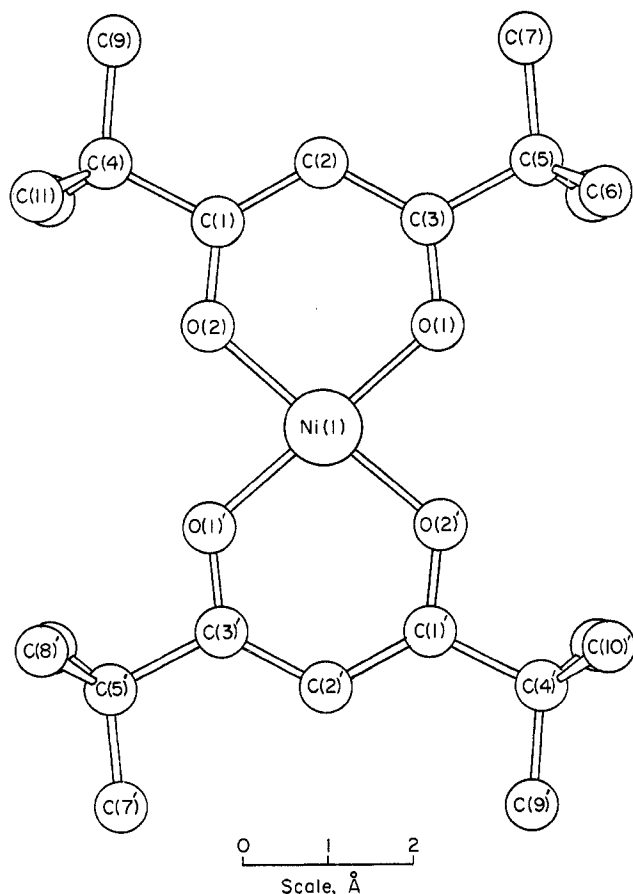


Figure 1.—The Ni(DPM)₂ molecule projected onto the mean molecular plane. The numbering of the atoms corresponds to that in Tables I, III, and IV.

map. Further refinement was made in which positional parameters and anisotropic temperature factors were varied. On the first cycle of refinement the weighted residual fell to 0.151.

After some unsuccessful attempts to locate hydrogen atoms were abandoned, full-matrix refinement, varying all parameters, though not all on every cycle, was resumed. When the weighted residual had dropped to 0.12, positional parameters had ceased to change significantly and a difference Fourier map showed no anomalies. It was noticed only later that, apparently due to an overflow problem in the computer, standard deviations of the temperature factors were not obtained. It was not deemed worthwhile to resume computations to obtain these. It should be noted that due to the neglect of absorption corrections, the anisotropic temperature factors are not to be taken as having strict physical significance. Undoubtedly, they have compensated for some of the absorption errors. The six carbon atoms of the *t*-butyl groups presumably do have high temperature parameters due to librational motion, but not so high as those obtained for C(6) and C(7). It should then also be true that the calculated standard deviations are underestimates, by perhaps a factor of 2.

The final coordinates and thermal parameters are reported in Table I. The calculated structure factors

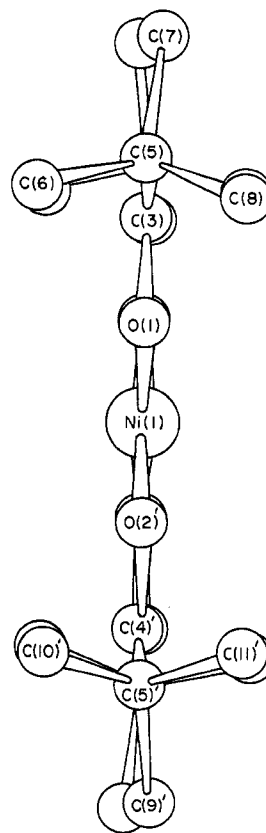


Figure 2.—The Ni(DPM)₂ molecule projected onto a plane perpendicular to the mean molecular plane. The nearly perfect planarity of the molecular skeleton (*i.e.*, all atoms but methyl carbon atoms) is evident.

given by these parameters and the observed values are given in Table II. Three low-order structure factors were believed to suffer from extinction and were excluded from the final refinement. These are indicated by an asterisk in Table II. The structure factors in the table are scaled up from the true structure factors in electrons by a factor of 59.4.

Discussion

Molecular Structure.—The chelate rings and, indeed, the whole molecule were found to be essentially planar. A projection of the molecule onto the mean plane of the chelate ring is shown in Figure 1. The atoms are numbered according to the system used in the tables. Atoms with a prime are related to the unprimed atoms by a center of symmetry at the nickel atom. Figure 2 shows a projection of the molecule onto a plane perpendicular to the plane of the chelate ring and passing through the Ni and C(2) atoms. In this projection the orientation of the two independent *t*-butyl groups can be clearly seen. Both *t*-butyl groups have about the same orientation with respect to the chelate ring. In each of the two groups one carbon atom, C(7) and C(9), lies close to the plane of the ring. It is interesting to note that the orientation with respect to the ring of the *t*-butyl group in Ni(DPM)₂ is just the reverse (*i.e.*, $\sim 180^\circ$ rotation about the threefold axis of the *t*-butyl group) of that found⁷ in Zn(DPM)₂. In the case of Zn(DPM)₂ it is proposed

that the observed orientation is the result of minimization of interaction between the ring hydrogen atom and the methyl groups. Apparently in $\text{Ni}(\text{DPM})_2$ other considerations are dominant. One possible explanation may be minimization of intramolecular repulsions between *t*-butyl groups attached to opposite chelate rings. If the *t*-butyl groups were rotated 180° , the shortest distance between the methyl groups would be ~ 3.5 Å (*vs.* ~ 5.5 Å in the observed orientation). The generally accepted van der Waals radius for a methyl group is 2 Å. Barring packing considerations, it would seem likely that the observed orientation of the *t*-butyl groups is the result of minimization of intramolecular contacts between methyl groups on opposite ligands.

A calculation of all intermolecular distances up to 5.5 Å was made.²⁰ The list of all nearest intermolecular contacts in Table III shows that the intermolecular contacts are all on the order of the usual van der Waals lengths or greater. Some of the methyl group-methyl group contacts, however, are somewhat shorter than the usually accepted value of 4 Å, but no significance is attached to this. Further discussion will be restricted to intramolecular parameters.

TABLE III

SHORTEST INTERMOLECULAR DISTANCES	
Nearest neighbors	Distance, Å
Ni-C(9)	3.78
O(1)-C(9)	3.90
O(2)-C(9)	3.58
C(1)-C(10)	3.91
C(2)-C(6)	4.05
C(3)-C(10)	4.25
C(4)-Ni	4.46
C(5)-C(6)	4.54
C(6)-C(7)	3.92
C(7)-C(8)	3.65
C(8)-C(7)	3.65
C(9) ^a -O(2)	3.58
C(10) ^b -O(2)	3.73
C(11)-C(8)	4.01

^a Distance to nearest methyl C(10) = 3.77 Å. ^b Distance to nearest methyl C(11) = 4.09 Å.

From the parameters in Table I, the intramolecular bond lengths and angles were calculated.²¹ The bond lengths and angles and their averages over chemically equivalent but crystallographically independent bond lengths and angles are listed in Tables IV and V. It was found that all chemically equivalent bonds and angles except for the angles within the *t*-butyl groups were equivalent to within three standard deviations from their mean. While the average of the angles within the *t*-butyl groups was close to that expected for a tetrahedral array, several angles showed significant deviations from the mean. These deviations are probably the result of packing stresses.

The essential planarity of the entire chelate ring was

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TABLE IV
BOND LENGTHS IN ASYMMETRIC UNIT

	Length, Å
Nickel-Oxygen	
Ni-O(1)	1.836 ± 0.007
Ni-O(2)	1.836 ± 0.007
Av.	1.836 ± 0.005
Oxygen to Ring Carbon	
O(1)-C(3)	1.299 ± 0.013
O(2)-C(1)	1.328 ± 0.014
Av.	1.314 ± 0.010
Ring Carbon to Ring Carbon	
C(1)-C(2)	1.380 ± 0.017
C(3)-C(2)	1.399 ± 0.017
Av.	1.390 ± 0.012
Ring to <i>t</i> -Butyl Carbon	
C(1)-C(4)	1.527 ± 0.016
C(3)-C(5)	1.502 ± 0.019
Av.	1.574 ± 0.012
<i>t</i> -Butyl Carbon-Carbon	
C(5)-C(6)	1.455 ± 0.025
C(5)-C(7)	1.486 ± 0.026
C(5)-C(8)	1.524 ± 0.034
Av.	1.488 ± 0.016
C(4)-C(9)	1.545 ± 0.014
C(4)-C(10)	1.486 ± 0.022
C(4)-C(11)	1.510 ± 0.020
Av.	1.514 ± 0.011

TABLE V

BOND ANGLES IN ASYMMETRIC UNIT

	Angle, deg
Ring Angles	
O-N-O	94.6 ± 0.4
Ni-O(1)-C(3)	128.0 ± 0.8
Ni-O(2)-C(1)	126.2 ± 0.7
Av.	127.1 ± 0.5
O(2)-C(1)-C(2)	124.5 ± 1.3
O(1)-C(3)-C(2)	123.3 ± 1.3
Av.	123.9 ± 0.9
C(1)-C(2)-C(3)	123.1 ± 1.3
Ring to <i>t</i> -Butyl Angles	
C(2)-C(3)-C(5)	124.4 ± 1.1
C(2)-C(1)-C(4)	123.8 ± 1.2
Av.	124.1 ± 0.8
<i>t</i> -Butyl Angles	
C(3)-C(5)-C(6)	113.4 ± 1.4
C(3)-C(5)-C(7)	114.0 ± 1.5
C(3)-C(5)-C(8)	109.5 ± 1.1
C(7)-C(5)-C(8)	102.7 ± 1.6
C(6)-C(5)-C(8)	106.0 ± 1.5
C(6)-C(5)-C(7)	110.4 ± 1.6
Av.	109.3 ± 0.6
C(1)-C(4)-C(9)	109.8 ± 0.9
C(1)-C(4)-C(10)	104.9 ± 1.1
C(1)-C(4)-C(11)	109.1 ± 0.9
C(9)-C(4)-C(10)	111.1 ± 0.9
C(9)-C(4)-C(11)	109.0 ± 0.9
C(10)-C(4)-C(11)	112.8 ± 0.9
Av.	109.4 ± 0.4

checked quantitatively by computing the "best plane" using least squares for the OCCCO and the plane of the OMO portions of the ring. The dihedral angle between the OMO and mean OCCCO planes was $179.5 \pm 0.5^\circ$. No atom falls more than three stand-

TABLE VI
COMPARISON OF MOLECULAR DIMENSIONS OF CHELATE RINGS IN SOME
SELECTED β -DIKETOENOLATE COMPLEXES

Compound	Bonds in ring, Å			C_{ring} Caliph	Angles in ring, deg				Dihedral angle ^a	Ref
	M-O	C-O	C-C		OMO	MOC	OCC	CCC		
Four-Coordinate Planar										
Ni(DPM) ₂	1.836	1.314	1.390	1.514	94.6	127.1	123.9	123.1	179.5	
Cu(acac) ₂	1.92	93.5	178	22
Four-Coordinate Tetrahedral										
Zn(DPM) ₂	1.962	1.274	1.405	1.157	94.7	121.8	125.8	127.0	180	12
Five-Coordinate										
Zn(acac) ₂ ·H ₂ O	2.02	1.291	1.395	1.510	88.5	127.1	124.2	125.9	168	31
VO(acac) ₂	1.97	1.285	1.397	1.52	87.5	129.1	123.7	123.8	168	33
Six-Coordinate Monomeric										
Co(acac) ₂ ·2H ₂ O	2.055	1.275	1.420	1.48	92.0	123.4	124.9	127.9	164	27
Ni(acac) ₂ ·2H ₂ O	2.015	1.272	1.412	1.510	92.4	123.5	125.5	126.6	167	35
Six-Coordinate ^b Polymeric										
[Co(acac) ₂] ₄	2.055 2.210	1.277	1.469	1.565	168	29
[Co(acac) ₂ ·H ₂ O] ₂	2.021	1.245	1.421	172	28
[Ni(acac) ₂] ₃	2.01	1.33	1.55	2
Eight-Coordinate										
Zr(acac) ₄	2.198	1.270	1.399	1.517	75.0	133.1	123.7	127.5	158	34

^a Angle in degrees between OMO plane and mean plane through OCCCO. ^b Second entry in M-O column is metal to shared oxygen bond length.

ard deviations out of the "best" plane for the entire ring.

It has been observed in all of the structural determinations on metal complexes with β -ketoenolates that the OCCCO portion of the ring is planar or almost planar. The OMO plane, however, is often canted to the mean plane of the ligand atoms. It has been shown⁷ that while this tendency is common it is not a necessary condition. In the structural determination on Zn(DPM)₂ it was found that the entire chelate ring was required to be rigorously planar on the basis of crystallographic symmetry of the space group. It is apparent from inspection of the dihedral angles listed in Table VI that only in the four-coordinate complexes are the chelate rings planar. All of the more highly coordinated complexes have dihedral angles between ~ 158 and $\sim 172^\circ$. Specific explanations, based on various kinds of intermolecular interactions, have been proposed in individual cases, but it may be that a more general discussion could be given based upon intramolecular forces.

Comparison of Results to Those for Other β -Ketoenolates and Related Metal Complexes.—Metal complexes with β -ketoenolates have been studied by X-ray diffraction^{1,7,22-36} previously. A comparison of the

results of this work with other three-dimensional work of comparable accuracy is shown in Table VI. Results for the carbon-oxygen, ring carbon-ring carbon, and ring carbon-aliphatic carbon bond lengths are consistent with prior results. As has already been pointed out,⁷ these bond lengths correspond to bond orders of ~ 1.3 , ~ 1.5 , and ~ 1.0 , respectively, due account being taken for shortening on going from sp^3 to sp^2 hybridization. These bond orders are consistent with the assumption of delocalized π bonding in dipivaloylmethanide and acetylacetonato rings.

Nickel-Oxygen Bond Lengths.—A point of particular interest is the mean Ni-O bond length, 1.836 ± 0.005 Å, as compared to Ni-O bond lengths in other Ni(II) complexes, particularly the closely related [Ni(acac)₂]₃ and Ni(acac)₂(H₂O)₂, in which the distances from Ni to nonbridging oxygen atoms are 2.01 ± 0.07 and 2.015 ± 0.01 Å, respectively. There are at least three possible explanations for this, no one of which excludes the others. One possibility is that the donor ability or basicity of the oxygen atoms in the DPM ion is much greater than that for the oxygen atoms in acac⁻ because of the greater electron-donating effect of the *t*-butyl group compared to methyl groups. While this may make some contribution to the observed shortening, we doubt that it can account for more than a small fraction of it. A second effect which might operate in the right direction, but which is also considered likely to be small, is the possibility of metal-oxygen π bonding in the planar molecule by means of the metal p_z orbital.

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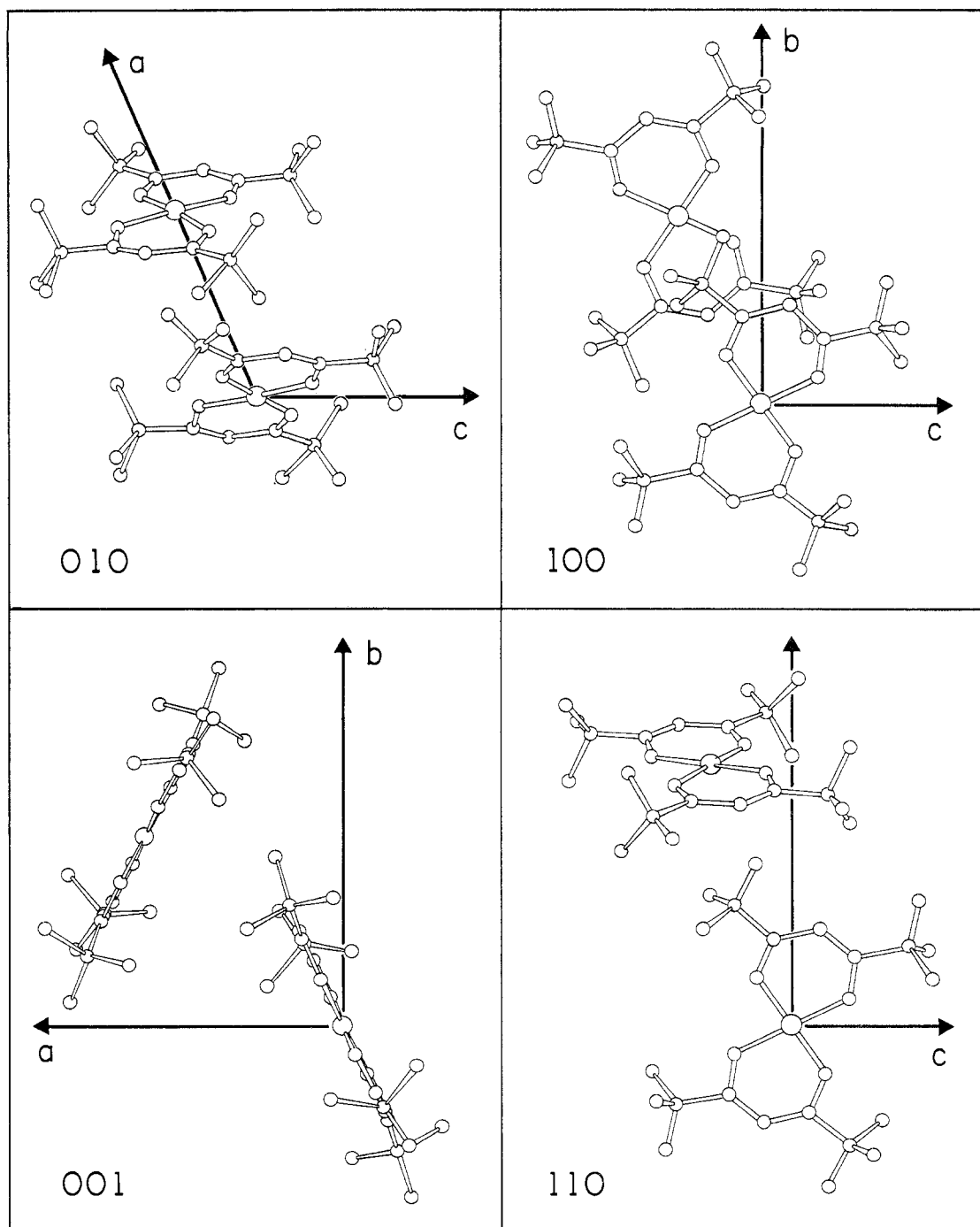


Figure 3.—Projections of the $\text{Ni}(\text{DPM})_2$ molecules on four crystal planes.

We believe that the main cause of the short metal-oxygen bonds here as compared to those in the molecules containing octahedrally coordinated $\text{Ni}(\text{II})$ is the absence of electrons from the d orbital which is σ antibonding with respect to the $\text{Ni}-\text{O}$ interactions. The octahedrally coordinated complexes contain high-spin nickel(II) and the two d orbitals which are antibonding in respect to the $\text{Ni}-\text{O}$ bonds, namely $d_{x^2-y^2}$ and d_{z^2} , are each occupied by one electron. In the low-spin square complex, however, the d orbital which is antibonding in respect to the $\text{Ni}-\text{O}$ bonds, namely d_{xy} in the coordinate system used here, is empty. There are two main reasons for preferring this explana-

tion, or at least assuming that it represents the predominant effect.

First, the shortening effect observed here is very similar to those which occur in other cases where one or both of the first two factors mentioned are not operative.

Thus, for example, the $\text{Ni}-\text{N}$ distances in the paramagnetic bis(*meso*-stilbenediamino)diaquonickel(II) complex are 2.05 Å, whereas those in the corresponding anhydrous, diamagnetic complex are 1.89 Å.³⁶ The ligand stilbenediamine cannot engage in π bonding. Thus only the third factor, the change in the population of the antibonding $d\sigma$ orbital, could apply here. Also,

the Ni-O bond lengths in three planar salicylaldimino complexes³⁷⁻³⁹ of Ni(II) are in the range 1.80-1.84 Å, whereas in bis(salicylaldehydato)diaquonickel(II)⁴⁰ the Ni-O distances are 2.03 Å. The only explanation which seems to apply to all cases, in all of which the effects are of similar magnitude, is the one concerned with changes in d orbital population.

Second, the magnitude of the shortening effect, 0.15-0.20 Å per change of one electron in a d orbital which is antibonding with respect to four ligands, is comparable with the changes in octahedral radii of divalent metal ions of the first transition series as electrons are added to the e_g orbitals.⁴¹ Thus, $R(\text{Mn}^{2+}) > R(\text{V}^{2+})$ by ~ 0.25 Å, where two e_g electrons per six ligands have been added, but where the concomitant increase in nuclear charge tends to diminish the effect by about 0.05 Å.

Orientation of Molecules in the Unit Cell.—One important purpose for undertaking this crystal structure determination was to ascertain the orientation of the molecules in the unit cell and to calculate therefrom the relationship of the molecular axes to the various well-developed faces of the crystals. Such data were necessary for the study of the polarized crystal spectra of both the nickel and the isomorphous copper compounds and for the study of the esr spectrum of Cu-(DPM)₂ using Ni(DPM)₂ as host. The spectroscopic investigations will be reported later.

Figure 3 shows the projections of the molecules on the 010, 001, 100, and 110 crystal planes. Table VII gives orthogonal coordinates for each of the two molecules relative to axes defining two of the principal planes, *viz.*, $a, b, \perp a$ (001) and $c, b, \perp c$ (100). These are particularly useful in making the quantitative calculations required to resolve polarized spectra into polarizations appropriate to the internal molecular Cartesian coordinates.

A few particular observations concerning the orientations of the molecules may be made. Since the two molecules are related by a twofold screw axis parallel to b , they have identical projections on the 010 plane,

TABLE VII
ORTHOGONAL COORDINATES FOR ALL ATOMS
IN ASYMMETRIC UNIT

	$a, b, \perp a$ coordinates, Å			$c, b, \perp c$ coordinates, Å		
	a	b	a	c	b	c
Atoms of Molecule 1						
Ni	0.000	0.000	0.000	0.000	0.000	0.000
O(1)	-0.306	0.785	1.631	1.619	0.785	0.363
O(2)	0.921	1.434	-0.683	-0.992	1.434	0.577
C(1)	1.164	2.580	-0.058	-0.513	2.580	1.046
C(2)	0.773	2.863	1.235	0.829	2.863	1.198
C(3)	0.108	1.942	2.051	1.841	1.942	0.910
C(4)	1.944	3.551	-0.941	-1.633	3.551	1.414
C(5)	-0.369	2.233	3.445	3.311	2.233	1.021
C(6)	-1.814	2.152	3.590	4.015	2.152	-0.249
C(7)	0.136	3.514	4.001	3.622	3.514	1.706
C(8)	0.208	1.301	4.405	3.965	1.201	1.931
C(9)	2.113	4.902	-0.210	-1.027	4.902	1.858
C(10)	3.259	2.894	-1.162	-2.355	2.894	2.535
C(11)	1.180	3.778	-2.224	-2.510	3.778	0.206
Atoms of Molecule 2						
Ni	5.850	5.490	0.000	-2.309	5.490	5.375
O(1)	5.544	4.706	1.631	-0.689	4.705	-5.738
O(2)	6.771	4.056	-0.683	0.301	4.056	5.952
C(1)	7.014	2.910	-0.058	-2.822	2.910	6.421
C(2)	6.623	2.627	1.235	-1.480	2.627	6.573
C(3)	5.958	3.548	2.051	-0.468	3.548	6.285
C(4)	7.794	1.939	-0.941	-3.942	1.939	6.789
C(5)	5.481	3.258	3.445	1.002	3.257	6.400
C(6)	4.036	3.338	3.590	1.706	3.338	5.125
C(7)	5.986	1.976	4.001	1.313	1.976	7.081
C(8)	6.058	4.289	4.405	1.656	4.289	7.306
C(9)	7.963	0.588	-0.209	-3.336	0.588	7.233
C(10)	9.109	2.596	-1.162	-4.664	2.596	7.909
C(11)	7.030	1.712	-2.224	-4.819	1.712	5.580

as is apparent in Figure 3. The dihedral angle between the mean planes of the two molecules is $44.9 \pm 0.9^\circ$, while the line passing through Ni and the carbon atoms C(2) and C(2)' (which we shall later identify with the molecular x axis in molecular orbital calculations and the interpretation of spectra) makes an angle of $24.2 \pm 0.8^\circ$ with the b axis of the unit cell. This is most clearly shown in the 001 projection (Figure 3).

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