PF_3 and $(C_2F_5)_2PF_3$, which do show n.m.r. spectroscopic equivalence of PF fluorine atoms. Recently, it has been shown that the triphenylphosphine groups in $[(C_6H_5)_3P]_3RhHCO$ are at equatorial positions.[28] The seemingly anomalous position of the hydrogen atom at an apical site may, in fact, be a reflection of large repulsions between $(C_6H_5)_3P$ groups.

The low barrier to intramolecular exchange in Cl_2PF_3 makes a stronger case for our earlier contention that positional exchange will be a common, low-energy process in five-coordinate structures. Primarily this is a reflection of the small energy difference between a trigonal bipyramid and a tetragonal pyramid. We feel that, in general, a trigonal bipyramid or a slightly distorted version of it will best describe the ground state for five-coordinate species with monodentate ligands (gaseous, solution, or liquid state)[29] with a close-lying vibronically-excited state of tetragonal pyramid geometry. The potentially facile process for intramolecular ligand exchange in five-coordinate structures makes it unlikely that geometrical isomers in a substituted MX_5 species could be isolated by conventional techniques. It is notable that the very sensitive n.m.r. technique has given no evidence of isomers in our present and earlier work.[1] Moreover, gas chromatographic analysis of the various alkyl- and arylphosphorus(V) fluorides has failed to give evidence of geometrical isomers.

Experimental

All F^{19} spectra were recorded at 56.4 Mc. on a Varian Model V4300 high resolution spectrometer and associated magnet, and the H^1 spectra on a Varian A-60 spectrometer. Calibration of spectra was effected by superposition of an audiofrequency on the sweep field to produce side-band peaks. The external reference, for the F^{19} spectra, was trifluoroacetic acid.

All of the compounds described in this report were prepared by literature procedures and purified by distillation or recrystallization. Transfer of all volatile reagents was effected in a vacuum system. The synthesis of the compounds $(C_2H_5)_2NPF_4$ and $[(C_2H_5)_2N]_2PF_3$ will be reported separately.[30]

Acknowledgment.—We wish to thank Dr. W. R. Hertler for preparing the sample of pentaphenylphosphorus and Professor R. C. Lord for helpful discussions.

[28] S. J. LaPlaca and J. Ibers, *J. Am. Chem. Soc.*, **85**, 3502 (1963).

[29] Packing forces in the solid state may be large with respect to the energy difference between a trigonal bipyramid and a tetragonal pyramid. Therefore, there is the possibility that the geometry in the solid state may differ from that in the liquid or gasous state.

[30] R. Schmutzler, to be published.

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The Crystal Structure of Dibromo-2,5-dimethylpyrazinenickel(II) ($NiBr_2(CH_3)_2N_2C_4H_2$)

BY F. D. AYRES, PETER PAULING, AND G. B. ROBERTSON

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The crystal structure of the bright purple diamagnetic compound dibromo-2,5-dimethylpyrazinenickel(II) has been analyzed from two-dimensional X-ray diffraction data. Crystals are monoclinic, space group C2/m, $a = 9.09$, $b = 8.20$, $c = 6.52$ Å., $\beta = 108° 36'$, two formula units per unit cell. The structure consists of infinite chains of (2,5-dmp)$NiBr_2$ along the c-axis, the nickel atoms being linked to each other *via* the nitrogen atoms of the pyrazine ring. The coordination of the nickel atom is square-planar with nickel site symmetry 2/m. The bromine atoms are 2.31 Å. from the nickel atom along the twofold axis (b) perpendicular to the plane of the pyrazine groups.

Introduction

As part of a general study of pyrazine metal compounds, Lever, Lewis, and Nyholm[1] have recently prepared three intensely colored diamagnetic nickel(II) compounds. These are the compounds dibromo-2,5-dimethylpyrazinenickel(II) ((2,5-dmp)$NiBr_2$) and diiodo-2,5-dimethylpyrazinenickel(II), which are an intense purple color, and the analogous compound diiodo-2,6-dimethylpyrazinenickel(II), which is black. The compounds are diamagnetic, which would indicate that the coordination of the nickel atom is square-planar.[2]

Because most square-planar compounds of nickel(II) are yellow or red, it had been suggested that the intense color might result from a tetrahedral configuration, and, as pointed out by Lever, Lewis, and Nyholm,[1] the two configurations cannot be distinguished by means of the diffuse reflectance spectra. An X-ray diffraction analysis of (2,5-dmp)$NiBr_2$ was initiated in order to establish the molecular stereochemistry.

Experimental

The crystals decompose very rapidly in the presence of water vapor, and it was necessary to seal each crystal in a Lindemann glass capillary in a P_2O_5 drybox. This did not completely eliminate crystal degradation, but the rate was much reduced and changes as reflected in the apparent thermal parameters occurred only over periods of some weeks. Crystals of the compound show striking dichroism from purple to wine-red in, respectively, reflected and transmitted light.

Crystals are monoclinic, space group C2/m, $a = 9.09 \pm 0.01$, $b = 8.20 \pm 0.01$, $c = 6.52 \pm 0.01$ Å., $\beta = 108° 36'$, $Z = 2$ mole-

[1] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 5042 (1963).

[2] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960.

TABLE I

ATOMIC POSITION AND ISOTROPIC THERMAL PARAMETERS AND STANDARD DEVIATIONS FOR DIBROMO-2,5-DIMETHYLPYRAZINENICKEL(II)

Atom	X	Y	Z	B	σ_x	σ_y	σ_z	σ_B
Ni	0	0	0	2.02	0	0	0	0.17
Br	0	0.282	0	2.67	0	0.001	0	0.09
N	0.006	0	0.287	1.52	0.005	0	0.007	0.78
C_1	0.134	0	0.454	1.46	0.005	0	0.009	0.84
C_2	−0.132	0	0.332	1.42	0.005	0	0.008	0.82
C_3	0.290	0	0.412	2.60	0.006	0	0.010	1.12

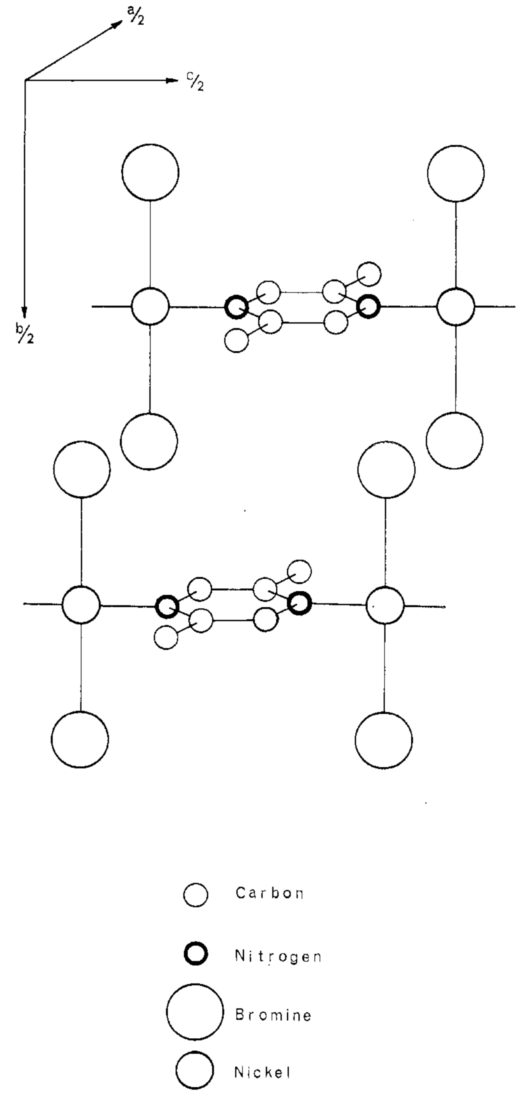

Fig. 1.—A diagram of the crystal structure of dibromo-2,5-dimethylpyrazinenickel(II) without hydrogens.

cules per unit cell, $\rho_{obsd} = 1.91$ g./cm.^{3} by pycnometer, $\rho_{calcd} = 1.931$ g./cm.^{3}, $F(000)$, the number of electrons in the unit cell, is 312. The cell dimensions were determined from Weissenberg and precession photographs calibrated with pure aluminum wire. Each of the crystals we have investigated was twinned about the c-axis, there being three twins (or triplets) in each crystalline group. The diffraction maxima from each component of the triplet were indexed in the usual way. The only systematic absences are of the type (hkl) with $h + k = 2n + 1$ corresponding to C centering; the allocation to space group C2/m is based on the observed 2/m molecular symmetry.

Multiple film equi-inclination Weissenberg photographs were taken with Cu Kα radiation of the zero, first, and second layers of the (001) zone. Zero-layer precession photographs were taken with Mo Kα radiation of the zones (010) and (100). Subsequently only the zero-layer Weissenberg data of (001) and the zero-layer precession data of (010) were used in the analysis and refinement of the structure.

The intensities of the Weissenberg photographs were estimated by eye with a calibrated film strip made with the crystal, and the precession photograph intensities were measured with a Joyce Loeble microdensitometer. The data were corrected only for Lorentz and polarization effects. The intensities of those planes whose diffraction maxima were overlapped by maxima from others of the triplet in each crystalline group were determined by careful estimates of the amount of each triplet present. These estimates were obtained by the measurement of the average relative intensities of equivalent but not overlapping maxima from the separate components.

Analysis and Refinement

The initial coordinates of all atoms were determined directly from the Patterson function projections (010) and (001). Refinement of over-all scale factor, position, and isotropic thermal parameters was done by least-squares analysis, all observations being given equal weight. The atomic scattering factor used for nickel(0) was from Watson and Freeman,[3] that for bromine from Freeman,[4] and those for carbon and nitrogen from Berghuis, *et al.*[5] The least-squares refinement scheme used was that of Rollett,[6] in which atomic position and isotropic thermal parameter shifts are obtained from a 4 × 4 block matrix in which all intraatomic parameter cross terms are included and the scale shift is obtained from a 2 × 2 matrix coupling the scale with an over-all temperature factor. Using only two-dimensional data it was necessary to use partial shifts to prevent oscillation.

Each of the two projections was refined independently. Satisfactory convergence was achieved following four cycles of least-squares calculation on each projection. The final position and thermal parameters are shown together with their estimated standard deviations in Table I. The listed z coordinates and temperature factors are weighted means of the values from the two projections using weights $\omega_i = 1/\sigma_i^2$ where σ_i is the estimated standard deviation for each parameter calculated with the expression[7]

$$\sigma_i^2 = a_{ii}\Sigma\Delta^2/(n - s)$$

In this expression a_{ii} is the diagonal element of the inverse 4 × 4 least-squares matrix $\Delta = |F_{obsd}| - |F_{calcd}|$,

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(3) R. E. Watson and A. J. Freeman, *Acta Cryst.*, **14**, 27 (1961).

(4) A. J. Freeman, *ibid.*, **12**, 261 (1959).

(5) J. Berghuis, J. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

(6) O. S. Mills and J. S. Rollett in "Computing Methods and the Phase Problem in X Ray Crystal Analysis," R. Pepinsky, J. M. Robertson, and J. C. Speakman, Ed., Pergamon Press, Oxford, 1961.

(7) International Tables for X Ray Crystallography, Volume II, The Kynoch Press, Birmingham, 1959.

n = the number of data, and s = the number of parameters. The listed standard deviations were determined with the relationship

$$\sigma_{\text{weighted}} = \sigma_1\sigma_2/(\sigma_1^2 + \sigma_2^2)^{1/2}$$

The refined thermal parameters were all systematically higher for the (001) projection than for the (010) projection. This is consistent with the progressive degradation of the crystal during the collection of the data, the photographs being taken in the order ($hk0$), ($hk1$), ($hk2$), ($h0l$), and ($0kl$). Values of the usual residual for the parameters listed in Table I are 0.075 for the 82 independent observed planes of the (010) projection and 0.12 for the 46 independent observed planes of the (010) projection. Observed and calculated structure factors for both projections for the parameters of Table I are listed in Table II.

Discussion

The crystal structure is shown diagrammatically in Fig. 1. The structure is polymeric and consists of infinite chains of alternate nickel dibromide groups and pyrazine groups along the c-axis. The plane of the pyrazine groups is perpendicular to the twofold b-axis and the bromine atoms are placed along this axis above and below the plane, consistent with the 2/m point symmetry. Each pyrazine is linked through opposite nitrogen atoms to two nickel atoms and each nickel atom to two pyrazine groups.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR THE UNIT CELL ($\times$10) FOR THE (010) ZONE AND THE (001) ZONE

h	k	l	F_{obsd}	F_{calcd}
0	0	1	1212	1292
0	0	2	1445	1513
0	0	3	1380	1403
0	0	4	1027	1002
0	0	5	779	694
0	0	6	655	555
0	0	7	570	465
0	0	8	303	224
2	0	−8	421	312
2	0	−7	610	484
2	0	−6	714	577
2	0	−5	933	811
2	0	−4	1078	1028
2	0	−3	1498	1413
2	0	−2	1520	1413
2	0	−1	1796	1718
2	0	0	1769	1778
2	0	1	1769	1791
2	0	2	1014	1046
2	0	3	1092	1101
2	0	4	987	1004
2	0	5	536	449
2	0	6	588	523
2	0	7	406	341
4	0	−8	496	378
4	0	−7	622	490
4	0	−6	656	535
4	0	−5	837	769
4	0	−4	1032	995
4	0	−3	1283	1232
4	0	−2	1064	1040
4	0	−1	1567	1524
4	0	0	1282	1274
4	0	1	1115	1168
4	0	2	851	957
4	0	3	783	809
4	0	4	658	657
4	0	5	478	479
4	0	6	294	289
0	2	0	230	176
0	4	0	1404	1458
0	6	0	252	317
0	8	0	291	340
0	10	0	285	328
1	1	0	728	755
1	3	0	1275	1333
1	5	0	−210	−103
1	7	0	790	810
1	9	0	−212	−73
2	2	0	−674	−513
2	4	0	947	939
2	8	0	148	154
2	10	0	193	196
3	1	0	302	272
3	3	0	862	878
3	5	0	−359	−256
3	7	0	620	609
3	9	0	−237	−152
4	0	0	1172	1269
4	2	0	−473	−439
4	4	0	685	722
4	6	0	74	2
4	8	0	94	101
5	1	0	105	111
5	3	0	557	593
5	5	0	−291	−253
5	7	0	466	459
5	9	0	−145	−138
6	0	0	903	1040
6	2	0	−188	−182
6	4	0	575	647
6	6	0	94	96
7	1	0	365	339
7	3	0	618	651
7	7	0	402	489
8	0	0	607	737
8	2	0	−47	−77
8	4	0	440	487
8	6	0	99	112
9	1	0	120	121
9	3	0	298	338
10	0	0	302	395
10	2	0	−57	−102
10	4	0	166	254

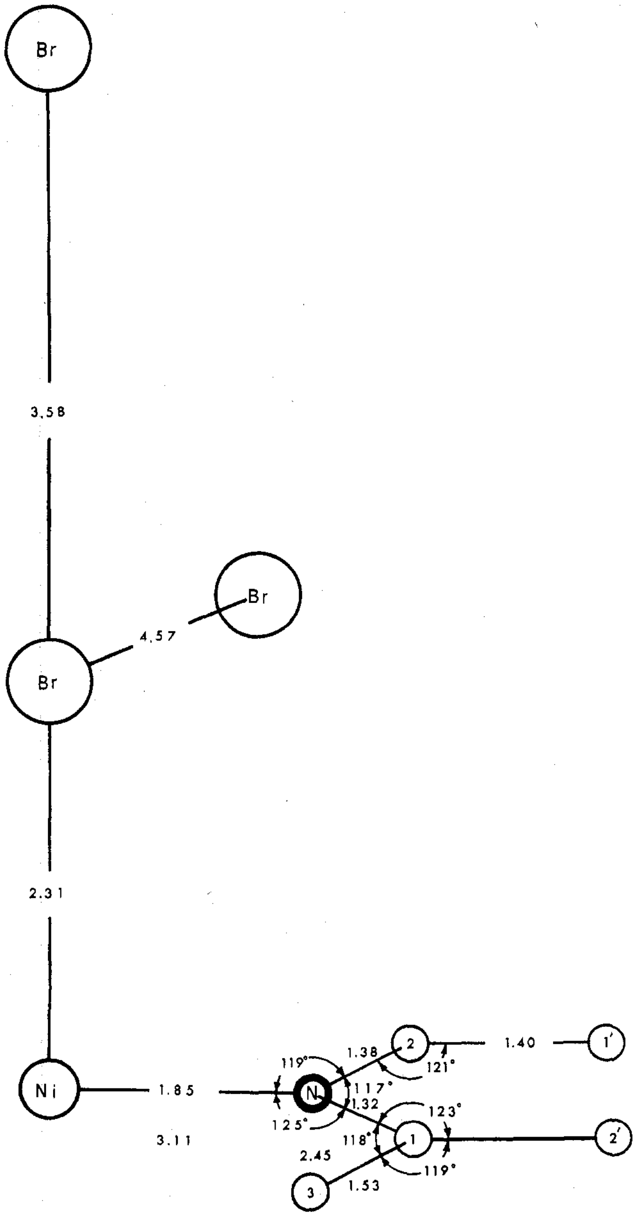

Fig. 2.—Interatomic distances and angles of dibromo-2,5-dimethylpyrazinenickel(II).

The observed square-planar configuration of nickel(II) in this compound is entirely consistent with the magnetic properties. The intense purple color of the compound is due to the conjugation of the chromophoric metal complexes through the linking aromatic systems, which shifts the normal indigo or blue absorption resulting in a yellow compound to an absorption in the green which gives a purple compound.

There are no intermolecular (from polymer to polymer) contacts (excluding hydrogen contacts) shorter than

3.58 Å. For square-planar coordination the crystal stereochemical arrangement with the metal halogen bonds directed perpendicular to the plane of the 2,5-dmp is that which would be expected and which results in minimum steric interaction between the methyl groups and the halogen atoms.

The nickel–ligand distances are shorter than might be expected. The Ni–Br distance 2.31 Å. is 0.2 Å. less than the sum of the bromine single bond radius and the octahedral covalent radius of nickel(II) applicable to the square-planar configuration (1.39 + 1.14 = 2.53 Å.).[2] The Ni–N distance at 1.85 Å. is also 0.2 Å. less than the sum of the appropriate radii (1.39 + 0.7 = 2.09 Å.). The Ni–N distance is, however, consistent with that found in dimethylglyoxime[8] (1.89 Å.) and in nickel phthalocyanine[9] (1.83 Å.). All other intramolecular interatomic distances and angles are shown in Fig. 2.

Acknowledgments.—We are grateful to Dr. B. Lever for presenting us with the problem and with crystals. We are also grateful to Mrs. Jean Dollimore, O. S. Mills, J. S. Rollett, and R. A. Sparks for making available computer programs. P. J. P. and G. B. R. are grateful to the U. S. Department of the Army through its European Research Office for support of this work.

[8] L. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

[9] J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 219 (1937).

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF NEW SOUTH WALES, SYDNEY, AUSTRALIA, AND THE DEPARTMENT OF INORGANIC CHEMISTRY, UNIVERSITY OF MELBOURNE, MELBOURNE AUSTRALIA

Magnetic Studies with Copper(II) Salts. VI. Variable Singlet–Triplet Energies in Amine-Substituted Copper(II) Alkanoates[1,2]

BY E. KOKOT AND R. L. MARTIN[3]

Received March 30, 1964

The magnetic susceptibility at temperatures between 80 and 350°K. is reported for a new series of monoamine adducts of copper(II) acetate and butyrate. Antiferromagnetic rather than Curie-type behavior is observed, from which the separation between singlet and triplet states of the dimeric species is deduced. Pyridine-type bases resemble water or dioxane in giving mono derivatives of copper(II) alkanoates with singlet–triplet separations of about 300 cm.$^{-1}$. In marked contrast, aniline-type bases reduce this interval to only 100 cm.$^{-1}$. The electronic spectra of these adducts in the region 8000–3250 Å. contain only the weak absorption bands at 7000 Å. (band I) and 3750 Å. (band II) generally observed for binuclear copper(II) alkanoates. The observed sensitivity of band I and insensitivity of band II to changes of the axially situated amine does not, at this stage, lead to the desired elucidation of the electronic spectrum.

Introduction

The copper(II) acetate monohydrate dimer, $Cu_2(CH_3CO_2)_4(H_2O)_2$, provides a singularly favorable example for testing current concepts of homopolar bonding by d electrons. The singlet ground state of the binuclear molecule is believed to arise predominantly from direct overlap of 3d–3d orbitals between pairs of contiguous copper atoms so that the ensuing d–d bond will have σ, π, or δ symmetry about the Cu–Cu internuclear axis. The bond is rather weak and measurements of the variation with temperature of magnetic susceptibility[4] and of paramagnetic resonance[5,6] establish that a triplet state for the molecule lies only some 300 cm.$^{-1}$ above the singlet ground state.

Figgis and Martin[4] recognized that the unusual geometric features of copper acetate coupled with the 3d^9 electron configuration of divalent copper conferred upon it favorable conditions for the formation of a unique class of metal-to-metal bond, namely a δ-bond. Support for this postulate was derived from estimates of the relevant overlap integrals. In particular, it was concluded that calculated overlaps were so small that the relative order of d orbital energies in the homonuclear diatomic species Cu_2^{4+} (for which the σ-bonding configuration about the Cu–Cu axis is certainly lowest; see Fig. 1) would almost certainly be inverted by the ligand field of ten neighboring oxygen atoms. This field was somewhat arbitrarily assumed to approximate to that of $[Cu(H_2O)_6]^{2+}$, the promotional energy of a positive hole $3d_{z^2} \leftarrow 3d_{x^2-y^2}$ being taken as 12,000 cm.$^{-1}$ after Polder.[7] A valence bond rather than molecular orbital description of the Cu–Cu binding was deliberately preferred as being more appropriate to the small magnitude of the overlap integrals involved.

The concept of δ-bonding in copper(II) acetate was strongly supported by Ross,[8] who demonstrated that

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[1] Part V of this series: R. L. Martin and H. Waterman, *J. Chem. Soc.*, 2960 (1959).

[2] This work is taken from a thesis presented by E. Kokot to the School of Chemistry, University of New South Wales, in partial fulfillment of the requirements for the Ph.D. degree, March, 1961.

[3] Department of Inorganic Chemistry, University of Melbourne, Melbourne, Australia.

[4] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, 3837 (1956), and references given therein.

[5] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.* (London), **A214**, 451 (1952).

[6] H. Abe and J. Shimada, *Phys. Rev.*, **90**, 316 (1953).

[7] D. Polder, *Physica*, **9**, 709 (1942).

[8] I. G. Ross, *Trans. Faraday Soc.*, **55**, 1057 (1959).