Anal. Calcd. for $C_{40}H_{36}BFe_2O_4P$: C, 65.4; H, 4.9; Fe, 15.2; O, 8.7. Found: C, 67.05; H, 4.5; Fe, 14.2; O, 8.3.

Infrared Spectrum.—Metal carbonyl bands at 2038 (m), 2026 (s), 2015 (vs), 1992 (s), 1970 (vs), 1942 (m); other absorption bands at 3108 (w), 3102 (w), 3090 (w), 3050 (m), 3028 (w), 2998 (w), 2980 (w), 1578 (m), 1478 (m), 1426 (s), 1360 (w), 1288 (m), 1268 (w), 1247 (m), 1066 (m), 1061 (sh), 1030 (m), 1017 (w), 1000 (m), 947 (sh), 935 (m), 902 (m), 888 (w), 853 (w), 835 (sh), 742 (s), 734 (s), 709 (s), 620 (m), 614 (m), 606 (m), 581 (s), 568 (m), 505 (w), 482 (w), 466 (w), and 453 (w) cm.$^{-1}$.

N.m.r. Spectrum (Dimethyl Sulfoxide Solution).—Doublet at 4.54 τ (J_{HP} = 1.7 c.p.s.) and doublet at 8.11 τ (J_{HP} = 9.0 c.p.s.) due to the cyclopentadienyl and methyl protons, respectively.

Conductivity in Nitromethane.—Molar conductance values were 64.5 and 68.4 ohm.$^{-1}$ at concentrations 2.2 and 1.0 × 10^{-3} *M*, respectively.

Correspondence

The Structures of Bis-(4-amino-3-penten-2-ono)copper(II), -nickel(II), and -palladium(II) and Bis-(3-amino-1-phenyl-2-buten-1-ono)-copper(II) and -nickel(II)

Sir:

X-Ray examination of single crystals of the inner complex chelates of divalent Cu,[1] Ni,[2] and Pd[3] with 4-amino-3-penten-2-one has shown them to be isomorphous.

It has been suggested from measurements of the optical activity of the resolved *d* and *l* components of both the Cu(II) and Ni(II) compounds[4] that the arrangement of ligands around the central metal atom may be tetrahedral or distorted tetrahedral.

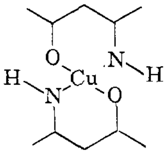
This possibility now becomes an unlikely one, Pd(II) compounds being square-planar as a rule, thus all three of the isomorphous compounds must be square-planar, or slightly distorted from it.

The unit cell is orthorhombic, space group Ccca, the following dimensions being measured: Ni, 16.7 × 15.1 × 13.5 Å., Cu, 16.9 × 15.2 × 13.8 Å., Pd, 17.2 × 15.2 × 13.4 Å.

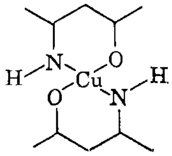
There are twelve molecules per unit cell, the calculated density of the Ni compound being 1.49 as compared with the measured density of 1.484.

Preliminary calculations have located the heavy atoms in the unit cell. Eight of the twelve molecules in the cell have their metal atoms located at the special positions (e)—*i.e.*, (x, $^1/_4$, $^1/_4$), etc.—of the space group,[5] with x = $^1/_3$. These positions have point symmetry 2, which means that the molecules must have a twofold axis of rotation about the central metal atom. This implies that the molecules have the *trans* configuration. The presence of the twofold axis does not allow us to distinguish between a planar or tetrahedral arrangement, however.

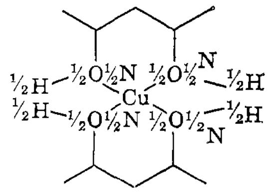
The remaining four molecules in the cell are located at the special positions (a), which have 222-point symmetry. A single molecule of this compound, no matter what configuration it takes, cannot have 222-point symmetry. This indicates that the molecules at these sites are disordered, having at random either one of two possible orientations. Thus, the average of



and



which can be written as



has 222-point symmetry about the metal atom.

It seems very plausible that disorder of this type should occur, as the two differently oriented molecules would be very similar from the viewpoint of molecular packing in the crystal.

The molecules are packed in the crystal in layers separated by approximately 2.9 Å., which also shows that if the molecules are not completely planar, they can be at most only slightly distorted from it.

The related chelates of divalent Cu and Ni with 3-amino-1-phenyl-2-buten-1-one have been prepared by Mr. N. P. Sweeny of these laboratories, and single crystals of these have been examined by X-ray diffraction methods. It has not been possible to prepare the Pd compound thus far.

The crystal structure of these compounds is much simpler than that of the chelates with 4-amino-3-penten-2-one. Crystals of the Cu and Ni chelates with 3-amino-1-phenyl-2-buten-1-one are isomorphous, belonging to the monoclinic space group $P2_1/c$. The Cu compound has the unit cell dimensions 6.52 × 13.13 × 12.50 Å., β = 123.8°.

There are two molecules in the unit cell. Thus the metal atoms can be placed at special positions (a) of the space group, with point symmetry $\bar{1}$. This implies that the molecules have the *trans* configuration and that the coordination of the metal atom with its four near neighbors is perfectly planar.

A more complete study of the two sets of isomorphous compounds described herein is in progress, with

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(1) H. F. Holtzclaw, Jr., J. P. Coleman, and R. M. Alire, *J. Am. Chem. Soc.*, **80**, 1100 (1958).

(2) R. D. Archer, *Inorg. Chem.*, **2**, 292 (1063).

(3) N. P. Sweeny, private communication, to be published.

(4) T.-M. Hseu, D. F. Martin, and T. Moeller, *Inorg. Chem.*, **2**, 587 (1963).

(5) International Tables for X-Ray Crystallography, Vol. 1, 1952.

the aim of locating the lighter atoms in the crystal structures.

Acknowledgment.—The author is indebted to Mr. N. P. Sweeny for submitting these compounds for X-ray examination and wishes to acknowledge helpful discussions with Mr. Sweeny and Dr. G. L. Simmons, both of these laboratories.

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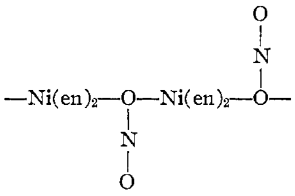
Bis-(2-methyl-1,2-diaminopropane)nickel(II) Nitrite Perchlorate—A Possible Interallogen Compound

Sir:

The red paramagnetic crystals obtained when bis-(ethylenediamine)nickel(II) perchlorate is crystallized from a solution containing sodium nitrite have been shown to be nitritobis(ethylenediamine)nickel(II) perchlorate, $[\mathrm{NiNO_2(en)_2}]\mathrm{ClO_4}$.[1] The cations lie in chains in which planar $\mathrm{Ni(en)_2}$ groups form axial bonds to one oxygen atom of linear nitrito groups, thus



$$-\mathrm{Ni(en)_2}-\underset{\substack{|\\ \mathrm{N}\\ |\\ \mathrm{O}}}{\mathrm{O}}-\mathrm{Ni(en)_2}-\overset{\substack{\mathrm{O}\\ |\\ \mathrm{N}\\ |}}{\mathrm{O}}-$$

To investigate the degree of interference that such a chain could tolerate, attempts were made to prepare analogous compounds by crystallizing bis(1,2-diaminopropane)nickel(II) perchlorate and bis-(2-methyl-1,2-diaminopropane)nickel(II) perchlorate from sodium nitrite solution. In the first case no crystalline product resulted, but in the second dark green crystals were obtained, with the unusual formula $\mathrm{Ni_3(NO_2)_2(C_4H_{12}N_2)_6(ClO_4)_4}$.

Anal. Calcd. for $\mathrm{C_{24}H_{72}Cl_4Ni_3N_{14}O_{20}}$: C, 24.1; H, 6.1; Ni, 14.7; N, 16.4; $\mathrm{NO_2^-}$, 7.7. Found: C, 23.7; H, 5.5; Ni, 14.6; N, 16.1; $\mathrm{NO_2^-}$, 7.8.

Magnetic susceptibility measurements made on the solid compound gave the results shown below.

Temp., °K.	298	195	90
$10^6\chi'_{\mathrm{m}}$	3006	4428	8690

χ'_{m} is the molar susceptibility after correction for diamagnetism. The Curie–Weiss law is obeyed ($\Delta = 20°$) and the magnetic moment is 2.78 B.M. per nickel atom. This value is low for a paramagnetic nickel complex and significantly lower than that obtained for $\mathrm{NiNO_2(en)_2]ClO_4}$, which was 3.23 B.M.

In crystals of the green form of bis(benzyldiphenylphosphine)dibromonickel(II),[2] one nickel atom out of three has been shown to lie on a center of symmetry and to have a square-planar bond configuration, whereas the other two nickel atoms have a tetrahedral bond configuration. The magnetic moment for the compound was again low (2.7 B.M.) on the assumption that all nickel atoms were equivalent, but when it was recognized that only two-thirds were paramagnetic the value for the atom was 3.3 B.M.

Crystals of bis-(2-methyl-1,2-diaminopropane)nickel(II) nitrite perchlorate are monoclinic, with $[a] = 13.46 \pm 0.05$, $[b] = 14.03 \pm 0.06$, $[c] = 13.33 \pm 0.05$ Å., $\beta = 94.2°$. The density by flotation in an ethylene dibromide–carbon tetrachloride mixture is 1.54 g. cm.$^{-3}$, hence there are two formula units (*i.e.*, six nickel atoms) per unit cell. Systematic extinctions occur for $h0l$ when $h + l$ is odd and for $0k0$ when k is odd, and the space group is then $\mathrm{P2_1/n}$. Symmetry demands that one-third of the nickel atoms lie on centers of symmetry, and these are crystallographically independent of the other nickel atoms. This situation exactly parallels that for bis(benzyldiphenylphosphine)dibromonickel(II), as does the color and the low apparent magnetic moment. If it were assumed that only two-thirds of the nickel atoms in bis-(2-methyl-1,2-diaminopropane)nickel(II) nitrite perchlorate were paramagnetic, their moment would be 3.37 B.M.

It is stoichiometrically impossible to propound a structure analogous to that of $[\mathrm{NiNO_2(en)_2}]\mathrm{ClO_4}$. An attempted two-dimensional structure analysis of bis-(2-methyl-1,2-diaminopropane)nickel(II) nitrite perchlorate was unsuccessful, but consideration of the three principal projections led to consistent coordinates for three heavy atoms, presumably the independent nickel atom and the two chlorine atoms. The closest approach of such a heavy atom to the nickel on the center of symmetry is 6 Å., and a trimeric structure analogous to that of bisacetylacetonatonickel(II)[3] is unlikely. It seems probable that this unusual compound is another example in which two stereochemically different bond configurations coexist, for which type of compound the name interallogen has been suggested.[2]

It is hoped to proceed to a three-dimensional X-ray analysis at a later date.

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(2) B. T. Kilbourne, H. M. Powell, and J. A. C. Darbyshire, *Proc. Chem. Soc.*, 207 (1963).

(3) G. J. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961).

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