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

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CONTRIBUTION NO. 283 G. E. GURR
CENTRAL RESEARCH LABORATORIES
MINNESOTA MINING AND MANUFACTURING COMPANY
ST. PAUL 19, MINNESOTA
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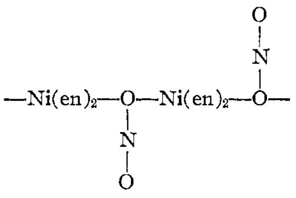
Bis-(2-methyl-1,2-diaminopropane)nickel(II) Nitrite Perchlorate—A Possible Interallogen Compound

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.

CHEMISTRY DEPARTMENT D. HALL
UNIVERSITY OF AUCKLAND J. M. WATERS
AUCKLAND, NEW ZEALAND

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