No evidence is obtained for the formation of the pentadentate complex here, although it is possible that small amounts of other complexes could be formed in solution and remain undetected.

Acknowledgment.—This work was supported by the National Research Council of Canada.

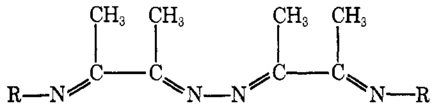
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
EARLHAM COLLEGE, RICHMOND, INDIANA 47374

Metal Complexes with Azine Ligands. III. Biacetyl Oxime Azine with Nickel(II)[1]

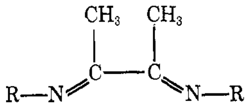
BY WILMER J. STRATTON* AND PAUL J. OGREN[2]

Received December 15, 1969

2-Pyridinecarbaldazine (abbreviated PAA) and 2-pyridyl methyl ketazine have been shown[1,3,4] to form an unusual series of complexes of the general formula $[M_2L_3]X_4$. Much evidence has been accumulated to show that these compounds contain a bridged dinuclear complex cation with symmetric bis-bidentate bonding of each ligand to the two metal ions. Recently, Ball and Blake[5] have reported magnetic studies of $Ni_2(PAA)_3X_4$ salts which demonstrate spin–spin interaction between the two metal ions, thus lending further support to the proposed structure. Exploratory work with a nonaromatic analog of 2-pyridinecarbaldazine and 2-pyridyl methyl ketazine, biacetyl hydrazone azine (I, "BHA"), demonstrated that it likewise forms 2:3 complexes of the formula $M_2(BHA)_3X_4$.[3c]



I, R = NH_2
II, R = OH
III, R = OCH_3



IV, R = OH
V, R = NH_2

As part of a continuing study of tetrafunctional azine ligands, we report here the synthesis of two new ligands related to I and a brief study of their complexing ability. Biacetyl oxime azine (II, "H_2BOA") was of interest because of its structural relationship to the well-known nickel reagent, dimethylglyoxime (IV, HDMG) which forms a highly stable 2:1 neutral complex with nickel(II) $[Ni(DMG)_2]$. This compound has been shown by X-ray crystallography to be planar with two hydrogen bonds between the ligands[6] and is diamagnetic as expected for a square-planar d^8 ion. Dimethylglyoxime also forms a paramagnetic 2:1 octahedral complex with nickel(II) involving two coordinated chloride ions and no hydrogen bonds $[Ni(HDMG)_2Cl_2]$.[7] Biacetyl oxime azine (II) is potentially capable both of forming hydrogen bonds and of bridging two metal ions.

A second new ligand, biacetyl methoxime azine (III), was of interest both because this ligand precludes the possibility of hydrogen bonding and because we wanted to investigate the steric effect of terminal methyl groups on complexing ability.

Experimental Section

Biacetyl Oxime Azine (II).—Eighteen grams of 2,3-butanedione 2-oxime (0.18 mol) (Eastman Chemical Co.) and 2.5 g of 97% hydrazine (0.08 mol) were added to 100 ml of ethanol and the solution was heated under reflux for 20 min. Upon cooling in ice, yellow crystals were deposited in 85% yield. The product was recrystallized in high yield from hot ethanol; mp 250–251°. *Anal.* Calcd for $C_8H_{14}N_4O_2$: C, 48.5; H, 7.1; N, 28.2. Found: C, 48.3; H, 6.9; N, 28.4.

Tetraaquobis(biacetyl oxime azine)dinickel(II).—Six-tenths gram of nickel(II) chloride hexahydrate (0.0026 mol) and 0.50 g of biacetyl oxime azine (0.0025 mol) were added to 50 ml of water. A 0.1 *N* sodium hydroxide solution was added slowly with rapid mechanical stirring until pH 11 was reached. The resulting brown solid was filtered, washed well with water, and dried; yield 0.40 g. The product has a very low solubility in water. *Anal.* Calcd for $Ni_2(C_8H_{12}N_4O_2)_2 \cdot 4H_2O$: C, 33.0; H, 5.5; N, 19.3; Ni, 20.2. Found: C, 33.4; H, 5.3; N, 19.7; Ni, 19.3, 19.8. The analysis also fits bis(dimethylglyoxime)-nickel(II) equally well. *Anal.* Calcd for $Ni(C_4H_7N_2O_2)_2$: C, 33.3; H, 4.9; N, 19.4; Ni, 20.3. The magnetic susceptibility was 2.9 BM per nickel ion.

Biacetyl Methoxime Azine (III).—This compound was prepared from 2,3-butanedione 2-methoxime (Eastman Chemical Co.) and hydrazine in ethanol. Recrystallization from hot ethanol gave yellow needles; mp 106–108°. *Anal.* Calcd for $C_{10}H_{18}N_4O_2$: C, 53.1; H, 8.0; N, 24.7. Found: C, 53.2; H, 8.1; N, 24.9. The compound gives no color change or other evidence of reaction when mixed with iron(II) or nickel(II) salts under a variety of conditions.

Equipment.—Magnetic susceptibility measurements were made with a Gouy balance, calibrated with $Hg[Co(NCS)_4]$. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer, calibrated with polystyrene film. A diffuse-transmission spectrum of the solid complex was recorded on a Beckman Model DB spectrophotometer, using a Nujol mull on filter paper.

pH Titrations.—These were carried out with an Orion 801 digital pH meter and a Corning combination glass–calomel electrode. Weighed samples of ligand (0.0100 mol) along with 25 ml of water and 15 ml of ethanol were placed in a small bottle, fitted with a four-hole stopper containing the electrode, the buret tip, and a nitrogen inlet tube. The bottle was also arranged for magnetic stirring. Nitrogen was swept through the mixture continuously to exclude CO_2. The mixtures were titrated with 4.88 *M* NaOH using a microburet. Similar titrations were carried out under the same conditions with appropriate amounts of nickel chloride added. In all four cases equilibration was slow in the region before the equivalence point, being especially bad for the titrations with nickel ion present. Readings were recorded after they had stabilized to ±0.01 pH unit

---

* To whom correspondence should be addressed.

(1) For the previous paper in this series, see W. J. Stratton, *Inorg. Chem.*, **9**, 517 (1970).

(2) Undergraduate research assistant, 1968.

(3) (a) W. J. Stratton and D. H. Busch, *J. Amer. Chem. Soc.*, **80**, 1286 (1958); (b) *ibid.*, **80**, 3191 (1958); (c) *ibid.*, **82**, 4834 (1960).

(4) W. J. Stratton, M. F. Rettig, and R. F. Drury, *Inorg. Chim. Acta*, **3**, 97 (1969).

(5) P. W. Ball and A. B. Blake, *J. Chem. Soc. A*, 1415 (1969).

(6) L. E. Godyski and R. E. Rundle, *Acta. Crystallogr.*, **6**, 487 (1953).

(7) A. G. Sharpe and D. B. Wakefield, *J. Chem. Soc.*, 496 (1957).

(±0.1 pH unit in the case of NiH_2BOA). Sodium ion corrections were applied above pH 13, using the chart provided with the electrode. No attempt was made to calculate equilibrium constants because of the very high ion concentrations.

Results and Discussion

Biacetyl oxime azine (II) reacts with nickel(II) in basic solution to produce a brown product of very low solubility. The analysis agrees with a formulation of $Ni_2(BOA)_2(H_2O)_4$ but also agrees equally well with $Ni(DMG)_2$. The latter could be a possbile product resulting from partial hydrolysis of HBOA, but the color, infrared spectrum, and magnetic susceptibility all indicate the product is not $Ni(DMG)_2$.

Selected infrared absorption bands are given in Table I for H_2BOA and its nickel complex, along with comparison data for dimethylglyoxime (IV), biacetyl dihydrazone (V), and their nickel complexes. Stoufer and Busch[8] have assigned the C=N stretch in biacetyl dihydrazone (BdH) and its complexes. Blinc and Hadzi[9] have assigned many of the bands in dimethylglyoxime complexes, including the C=N stretch and O—H stretch. The ligand of interest, H_2BOA, has bands in close agreement with the two reference ligands, as expected. The nickel complex of H_2BOA shows a shift to higher frequency for the azine C=N stretch and a shift to lower frequency for the oxime C=N stretch both of which are in agreement with the corresponding DMG and BdH complexes. This indicates tetracoordination of BOA, using all four nitrogen atoms. The OH band at 3213 cm^{-1} in HDMG is shifted in $Ni(DMG)_2$ to two weak bands at 2350 and 1780 cm^{-1} which Blinc and Hadzi[9] have assigned to stretching and bending modes, respectively, for the hydrogen-bonded OH. For H_2BOA the oxime OH band appears at 3100 cm^{-1}, but in the nickel complex this band disappears, with no weak bands appearing in the 2500–1600-cm^{-1} region, thus indicating no hydrogen bonding. The band at 3300 cm^{-1} is assigned to water.

TABLE I[a]

INFRARED STRETCHING VIBRATIONS IN THE REGION 4000–1600 CM^{-1}

	O—H	C=NN	C=NO
H_2BOA	3100 s	1598 s	1634 w
$Ni_2(BOA)_2(H_2O)_4$	(3300 s)[d]	1633 m	1600 w
HDMG	3213 s	. . .	1622 w
$Ni(DMG)_2$[b]	2350 w 1780 w	. . .	1560 s
BdH[c]	. . .	1582 m	. . .
$[Ni(BdH)_3]I_2$[c]	. . .	1613 s	. . .

[a] Abbreviations used: H_2BOA, biacetyl oxime azine; HDMG, dimethylglyoxime; BdH, biacetyl dihydrazone. [b] These results agree well with those of Blinc and Hadzi.[9] [c] See ref 8. [d] This band is assigned to H_2O, not the oxime.

As an aid to further understanding of the nickel(II)–biacetyl oxime azine system, pH titrations were carried out for the reaction of NaOH with the free ligand and with the ligand in the presence of 1 mol of nickel. Similar titrations were performed using dimethylglyoxime with and without the presence of 0.5 mol of nickel. The resulting curves (Figure 1) show clearly the increased acidity of the ligands in the presence of nickel ion. In the case of dimethylglyoxime, $pH_{1/2}$ changes from approximately 12.4 for the free ligand (curve A) to 1.2 for formation of the 2:1 neutral complex with loss of one proton per ligand (curve B). These results are in qualitative agreement with the careful studies of previous workers[10,11] using considerably more dilute solutions in dioxane–water mixtures. The dramatic increase in ligand acidity is attributed to the high stability of the hydrogen-bonded complex. The titration curve for biacetyl oxime azine (curve C) is similar to that of dimethylglyoxime except for a more pronounced break at 2 equiv of base, and shows $pH_{1/2}$ 12.7. In the presence of 1 mol of nickel per mole of H_2BOA (curve D) the graph shows one break for transfer of both protons, but $pH_{1/2}$ is considerably higher (approximately 5.1) than for the Ni–DMG system. We interpret these observations to indicate that the Ni–BOA complex contains no hydrogen bonds.

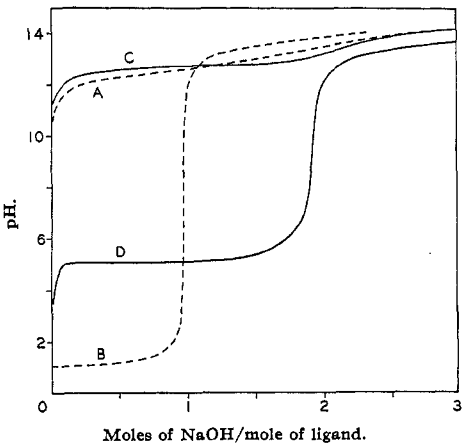


Figure 1.—pH titration curves for 4.88 *M* NaOH with (A) HDMG (10 mmol), (B) HDMG (10 mmol) and $NiCl_2$ (5 mmol), (C) H_2BOA (10 mmol), and (D) H_2BOA (10 mmol) and $NiCl_2$ (10 mmol).

The infrared, magnetic, and pH data all strongly suggest that the complex has a dimeric structure (VI) involving octahedral coordination about the nickel ions, symmetric bridging of the ligands, and no hydrogen bonds between the oxime ligands. The magnetic moment of 2.9 BM is slightly lower than normally observed for octahedral nickel but is in good agreement with data reported by Ball and Blake[5] for dinuclear nickel complexes involving a small amount of spin–spin interaction. The electronic spectrum of the solid complex (Nujol mull) has a major peak at *ca.* 24,000 cm^{-1} which is tentatively assigned to the $A_{2g} \rightarrow T_{1g}(F)$ transition. This is consistent with the proposed octahedral structure but is not consistent with either a tetrahedral or five-coordinate structure. No evidence was obtained for a dimeric coplanar 2:2 complex with

---

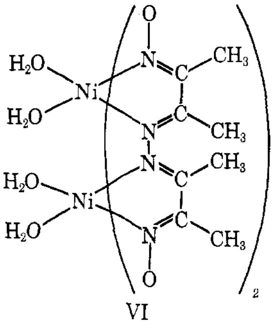
(8) R. C. Stoufer and D. H. Busch, *J. Amer. Chem. Soc.*, **82**, 3491 (1960).

(9) R. Blinc and D. Hadzi, *J. Chem. Soc.*, 4536 (1958).

(10) L. G. Van Uitert and W. C. Fernelius, *J. Amer Chem. Soc.*, **76**, 375 (1954).

(11) R. G. Charles and H. Freiser, *Anal. Chim. Acta*, **11**, 101 (1954).

hydrogen bonds at each end, analogous to $Ni(DMG)_2$. This may be attributed to interaction of the two central methyl groups which force twisting of the ligand in order to permit chelation with two metals.



VI

A second ligand, biacetyl methoxime azine (III), has been investigated for its complexing ability toward nickel. No evidence for any reaction with nickel was observed in neutral or basic solution. Examination of models reveals that the terminal methyl groups would create considerable steric strain if the ligands were coordinated to nickel in a manner similar to that in VI. This strain is apparently sufficient to prevent formation of stable complexes.

Acknowledgments.—This work was supported by the National Science Foundation (Grant No. 23490) and a Research Corp. departmental grant.

Contribution from the Allied Chemical Corporation,
Morristown, New Jersey 07960

Volatile Fluorinated Alkoxides of the Alkali Metals

By R. E. A. Dear,* W. B. Fox,
R. J. Fredericks, E. E. Gilbert, and D. K. Huggins

Received January 13, 1970

The fully fluorinated methoxides $CF_3O^-M^+$ have been reported, where M = K, Rb, or Cs.[1] These were found to be nonvolatile and to decompose at 80–100°; the fully fluorinated ethoxides, *n*-propoxides, isopropoxides, and *n*-butoxides were even less stable.[2] Among alkoxides of partially fluorinated alcohols, sodium hexafluoroisopropoxide, $(CF_3)_2CHONa$, has been reported to melt at 68°, with decomposition beginning at 110° and becoming violent about 170°.[3] Contrary to this report, we find that sodium hexafluoroisopropoxide, prepared by the action of sodium on the free alcohol, has a melting point of 114–116° and is, moreover, surprisingly volatile. Although the hexafluoroisopropoxide cannot be distilled at atmospheric pressure, the fact that it can be sublimed at 70° under vacuum is noteworthy for a compound of sodium; the corresponding lithium compound sublimes at 50° under vacuum. Trifluoroethanol and hexafluoro-2-propanol also form transition metal alkoxides which can be distilled or sublimed under reduced pressure.[4,5]

We have now found that perfluoro-*tert*-butyl alcohol forms lithium and sodium alkoxides which can be melted and distilled at atmospheric pressure, with no apparent change in composition. The perfluoro-*tert*-butoxides may be prepared either by reaction of the parent alcohol with the appropriate metal[6] or, more conveniently, by reaction of the alcohol with metal hydride in anhydrous ether: $(F_3C)_3COH + MH \rightarrow (F_3C)_3COM + H_2$ (M = Li, Na, K). That the lithium compound should show some volatility is not surprising since organolithiums are known to have considerable covalent chaacter.[7] The covalent character of sodium zirconium ethoxide also has been reported.[8] However, to our knowledge, this is the first example to be reported of a stable organosodium which survives distillation and is thus probably covalent rather than ionic.

The infrared spectra of lithium and sodium perfluoro-*tert*-butoxide (Nujol mulls) show the O–H region to be devoid of any absorbance, but sharp bands at about 1610–1616 cm^{-1} may be due to the C–O stretching frequency in $R_3C\text{–}OM$.[2] In contrast, the liquid phase spectrum of neat perfluoro-*tert*-butyl alcohol shows strong O–H stretching vibrations at 3704 and 3610 cm^{-1} and nothing further until the C–F region begins around 1400 cm^{-1}. The mass spectrum of sodium perfluoro-*tert*-butoxide (other salts were not examined) was complex and somewhat variable from one experiment to another, but the data clearly indicated the presence of polymeric species in the vapor. Samples examined with an AEI No. 902 mass spectrometer (source block 65°, ionizing potential 70 V) produced intense fragments containing from one to four sodium atoms associated with a varying number of C_4F_9O groupings, along with a plethora of lower breakdown fragments. A thorough investigation of the mass spectrometry of perfluoroalkoxide salts is in progress and will be reported at a later date.

Other alkoxides were examined briefly to see if they possessed similar properties. Potassium perfluoro-*tert*-butoxide and the sodium salt of $Cl_3CC(CF_3)_2OH$ were prepared and it was observed that although both compounds could be sublimed under reduced pressure in an ordinary vacuum sublimator, neither melted below 300° and both began to decompose at about 220°. Sodium chlorooctafluoro-*tert*-butoxide exhibited properties midway between those of the fully fluorinated sodium and potassium compounds, since distillation proved to be possible only on a microscale at atmospheric pressure and was accompanied even then by gas

---

* To whom correspondence should be addressed.

[1] M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).

[2] M. E. Redwood and C. J. Willis, *ibid.*, **45**, 389 (1967).

[3] H. J. Koetzsch, *Chem. Ber.*, **99**, 1143 (1966).

[4] P. N. Kapoor and R. C. Mehrotra, *Chem. Ind.* (*London*), 1034 (1966).

[5] P. N. Kapoor, R. N. Kapoor, and R. C. Mehrotra, *ibid.*, 1314 (1968).

[6] F. J. Pavlik, U. S. Patent 3,385,904 (1968) (3M Co.).

[7] G. E. Coates, "Organometallic Compounds," 2nd ed, Wiley, New York, N. Y., 1960, Chapter 1.

[8] W. G. Bartley and W. Wardlaw, *J. Chem. Soc.*, 422 (1958).