and a 46% yield of the new compound, *cis*-tetrafluoro(trifluoromethanolato)(trifluoromethylhydroperoxidato)sulfur.

**$CF_3OOSF_4OCF_3$.** Bp 43.9°; mp, glasses; mol wt 297.4, calcd 294.1; ir (in $cm^{-1}$) 1291 (s), 1276 (s), 1246 (vs), 1217 (s), 1172 (vs), 980 (m), 948 (vw), 919 (m), 862 (vs), 840 (vs), 740 (w), 702 (vw), 670 (w), 627 (w), 592 (m), 862 (vs), 840 (vs), 740 (w), 702 (vw), 670 (w), 627 (w), 592 (m), 568 (m), 520 (vw); nmr $CF_3{}^EOOSF_2{}^B(F)^A(F)^C$-$OCF_3{}^D$ $\phi^*$ (relative area, assignment) −70.07 (0.91, $SF^A$), −65.22 (2.10, $SF_2{}^B$) −57.10 (1.00, $SF^C$) 56.74 (3.03, $CF_3{}^DO$) 68.55 (2.97, $CF_3{}^EOO$), $J_{AB}$ = 147.4, $J_{AC}$ = 151.4, $J_{BC}$ = 149.2, $J_{AD}$ = 10.8, $J_{BD}$ = 10.8, $J_{BE}$ = 3.9, $J_{CE}$ = 3.9. The preceding represent the best fit *via* computer-assisted analysis of the experimental spectrum shown in Figure 1; $\log P(\text{mm}) = 7.0939 - 1066.8/T - 85260/T^2$; $\Delta H(\text{vap}) = 7.34$ kcal/mol; $\Delta S(\text{vap}) = 23.3$ eu. $\rho(t) = 1.856 - 0.003026t$. The mass spectrum was as expected for $CF_3OOSF_4OCF_3$.[16] In a test of the stability of this compound, a mixture of $(CF_3O)_2SF_4$ and $CF_3OOSF_4OCF_3$ was placed in 3.6 *M* NaOH. After 8 weeks at ambient temperature, appreciable quantities of both were recovered.

**Reaction of CO with $CF_3OOOCF_3$.** Reaction of CO with $CF_3OOOCF_3$ was carried out in a 75-ml vessel like that in the case of $SF_4$. $CF_3OOOCF_3$ (3.25) was condensed into the vessel. CO (3.15) was added and the vessel heated for 3 hr at 74°. After cooling the vessel to −196°, the noncondensables (0.63), presumably oxygen, were pumped off. The mixture of condensables was then subjected to glc at 31°. We found $COF_2$–$CO_2$ (1.64), $CF_3OOCF_3$ (1.52), $CF_3OOOCF_3$ (0.30), $CF_3OC(O)F$[20] (0.05), $CF_3OOC(O)F$[5,14] (0.33), $(CF_3O)_2CO$[21] (0.02), and $CF_3OOC(O)OCF_3$ (0.93). A trace of a slightly volatile solid was also observed in the mixture described above. Subsequent runs at higher pressures increased its yield and we were able to identify it as $[CF_3OC(O)]_2$.[22] The reaction gave a 29% yield of the new compound, bis(trifluoromethyl) peroxycarbonate.

**$CF_3OOC(O)OCF_3$.** Bp 25.0°; mp −80.0 to −81.3°; mol wt 213.0, calcd 214.0; ir (in $cm^{-1}$) 1878 (s), 1412 (vw), 1300 (s), 1250 (s), 1146 (vs), 1024 (s), 933 (m), 900 (m), 746 (m), 702 (m), 657 (vw) 607 (w), 580 (m), 471 (w); nmr $\phi^*$ (relative area, assignment) 59.31 (3.00, $CF_3O$), 69.50 (3.08, $CF_3OO$); $\log P(\text{mm}) = 6.8141 - 822.30/T = 104546/T^2$; $\Delta H(\text{vap}) = 6.97$ kcal/mol; $\Delta S(\text{vap}) = 23.4$ eu; $\rho(t) = 1.571 - 0.002747t$. The mass spectrum was as expected for $CF_3OOC(O)OCF_3$.[16]

**Other Reactions of $CF_3OOOCF_3$.** Reaction of $CF_3OOOCF_3$ with $H_2O$ and Hg for 6 hr at 22° was negligible and the trioxide was recovered unchanged. With $Cl_2$ at 70° quantitative decomposition of the trioxide to $CF_3OOCF_3$ and $O_2$ was observed after 18 hr and the $Cl_2$ was recovered unchanged.

**Acknowledgment.** This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation under Grant No. NSF-GP23098, and the Advanced Research Projects Agency, Propellant Chemistry Office, monitored by the Army Research Missile Command, Redstone Arsenal, Huntsville, Ala., under Contract No. DA-01-021-AMC-12264(Z). Invaluable assistance on nmr spectra was afforded by Dr. Joseph V. Paukstelis. A portion of this work was performed at Northeastern University, Boston, Mass. F. A. H. thanks Goodyear Atomic Corporation for a leave of absence during part of this work.

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# Crystal and Molecular Structure of a Salt of the (*o*-Benzoquinone diimine)tetracyanoiron(II) Ion

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**Abstract:** The two-electron oxidation product of *o*-phenylenediamine has been stabilized by coordination to low-spin iron(II) in the complex anion $[Fe(CN)_4(C_6H_4(NH)_2)]^{2-}$. The chemical and structural evidence conclusively demonstrates that the oxidation product contains stabilized *o*-benzoquinone diimine. We report here the three-dimensional single-crystal X-ray structure determination of the (*o*-benzoquinone diimine)tetracyanoiron(II) anion as the *N,N'*-dimethyl-1,4-diazabicyclo[2.2.2]octonium salt. The complex crystallizes with the orthorhombic space group $P2_12_12_1$ ($D_2{}^4$, No. 19) with cell dimensions $a$ = 14.526 (10), $b$ = 11.239 (8), $c$ = 12.724 (7) Å. There are four molecules of the complex per unit cell ($\rho_{obsd} = 1.40 \pm 0.01$ g cm$^{-3}$, $\rho_{calcd} = 1.423 \pm 0.002$ g cm$^{-3}$ for $Z$ = 4). All atoms including the hydrogen atoms have been located and their positional and thermal parameters refined by Fourier and least-squares techniques to a conventional $R$ factor of 5.6% for 4317 reflections. The average C–N distance in the *o*-benzoquinone ligand is 1.321 Å while the C–C distance of the α-diimine linkage is 1.443 Å. This result is consistent only with the α-diimine character expected of coordinated *o*-benzoquinone diimine.

Transition metal ions play an important role in the activation of coordinated ligands, enabling them to undergo various types of reactions and also stabilizing otherwise reactive species. Examples of this type of metal-assisted reaction are oxidative deamination and oxidative dehydrogenation of amine ligands; the course of the reaction is dependent on the nature of the metal ion involved. In oxidative deamination, an amine ligand in the presence of a labile transition metal ion and an appropriate oxidizing agent undergoes catalytic oxidation presumably facilitated by a higher unstable oxidation state of the metal ion. Deamination occurs during subsequent ligand dissociation and reaction with the solvent media.[2-4]

Oxidative dehydrogenation, on the other hand, occurs when an amine ligand is part of a complex that is stable to dissociation but which has an accessible higher oxidation state. The metal atom is oxidized to this

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(1) Author to whom correspondence should be addressed.

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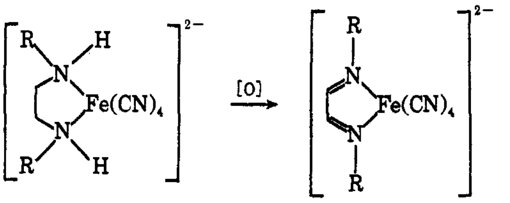
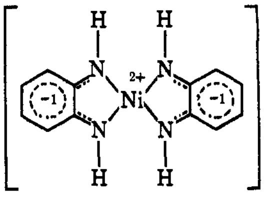
unstable higher state and subsequent metal–ligand intramolecular redox reactions result in the formation of an aldimine double bond which is stabilized by coordination with the metal ion.[5–9]

In macrocyclic ligand complexes in which the product of the ligand oxidation is a substitutionally inert metal complex such as low-spin d$^6$ Fe(II) or Co(III), the metal ion may have the capability of stabilizing otherwise reactive species. It has recently been found that low-spin iron(II) complex species containing aliphatic 1,2-diamines react with a variety of oxidizing agents to yield products containing either one or two aldimine functions, the latter being an α-diimine type ligand as shown below.[10]



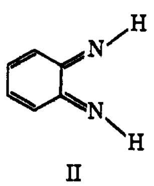
One of the complexes examined in this study of coordinated diamines, the tetracyano(*o*-phenylenediamine)iron(II) complex anion, was of special interest in view of the series of one-electron oxidation–reduction reactions of bis(*o*-phenylenediamine)–metal complexes which occur both chemically and electrochemically.[11] One unusual complex of that series is the product of the aerobic oxidation of bis(*o*-phenylenediamine)nickel(II) (I). This complex can perhaps be best described as



I

two spin-coupled $C_6H_4(NH)_2$ radical ions coordinated to Ni(II), giving a diamagnetic complex. The X-ray structure of this complex shows that it is planar (thus supporting the conclusion that the nickel is in the +2 and not in the 0 oxidation state), but it does not unequivocally establish the overall electronic structure of the complex.[12]

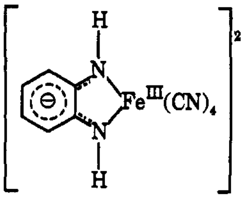
The terminal oxidation product of *o*-phenylenediamine, *o*-benzoquinone diimine (II), has been postulated



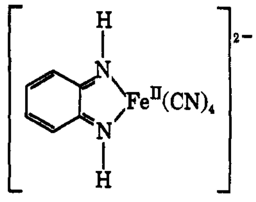
II

to exist in solution[13] but has never been isolated in any form. However, stabilization of this normally very reactive species should be possible by coordination to metal ions, such as iron(II), known to form very stable α-diimine complexes.

The oxidation of the yellow tetracyano(*o*-phenylenediamine)iron(II) dianion with molecular oxygen yields a very intensely colored purple product thought to contain the stabilized *o*-benzoquinone diimine ligand.[10] In view of the uncertainty of the electron distribution in the nickel complex (I) above, there is some question about the electronic structure of this intense purple product. It could, for example, conceivably be an d$^5$ iron(III) atom spin-coupled with a $[C_6H_4(NH)_2]^-$ radical ion (III) (which is formally identical with the *o*-phenylenediamine residue in the nickel complex (I)), or it could contain the terminally oxidized form of *o*-phenylenediamine, *o*-benzoquinone diimine, coordinated to d$^6$ low-spin iron(II) (IV). The single-crystal X-ray diffraction structure determination was accordingly undertaken to confirm the existence of the unusual *o*-benzoquinone diimine species and to compare its geometry with related α-diimine compounds.



III



IV

## Experimental Section

Tris(*o*-phenylenediamine)iron(II) perchlorate was prepared by the addition of ferrous perchlorate hexahydrate (Alfa Inorganics) to a methanol–ethanol solution of *o*-phenylenediamine (Baker, practical grade). Subsequent addition of sodium cyanide to the solution (under nitrogen) resulted in the substitution of four cyanide ions for two of the coordinated *o*-phenylenediamine molecules to yield the yellow, low-spin d$^6$ iron(II) complex, $Na_2[Fe(CN)_4(C_6H_4(NH_2)_2)]$.

Solutions of this compound are very sensitive to molecular oxygen and react rapidly with $O_2$ upon exposure to the atmosphere to yield the very intensely colored blue product, $Na_2[Fe(CN)_4(C_6H_4(NH)_2)]\cdot 4H_2O$. This complex is extremely stable and possesses many of the characteristics of hexacyanoiron(II) and tris(1,10-phenanthroline)iron(II) species, particularly in its stability toward dissociation and to attack by concentrated acids. Its reactions and solution behavior are quite similar to those found by Schilt for the α,α′-dipyridyltetracyanoiron(II) dianion.[14]

The complex is extremely soluble in water and attempts to isolate suitable crystalline samples from aqueous solutions as either sodium or potassium salts gave crystals containing large amounts of water of crystallization which were easily lost by efflorescence. According to Basolo[15] the counterion of choice is one which is the same size and has the same charge (of the opposite sign). For this reason we chose the *N*,*N*′-dimethyl-1,4-diazabicyclo[2.2.2]octonium ion as a more suitable cation than sodium or potassium. This cation was prepared by the method of Oae, Hovarth, Zalut, and Harris.[16] We shall hereafter refer to it as the dimethyl-Dabco[17] cation.

The Me$_2$-Dabco salt of the (*o*-benzoquinone diimine)tetracyanoiron ion forms fine, black, nearly octahedral crystals when precipitated from aqueous solution by the addition of methanol.

The space group was determined from zero and upper layer precession photographs to be $P2_12_12_1$ (systematic extinctions: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$). The density, measured by the flotation technique with carbon tetrachloride–dichloroethane solution, was $1.40 \pm 0.01$ g cm$^{-3}$. The cell con-

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(17) Dabco is the registered trademark of Houdry Processing Co. for 1,4-diazabicyclo[2.2.2]octane.

**Table I.** Crystal Data

Space group $P2_12_12_1$ ($D_2{}^4$, No. 19)
$Z = 4$
$a = 14.526 \pm 0.010$ Å
$b = 11.239 \pm 0.007$ Å
$c = 12.724 \pm 0.007$ Å
$\alpha = \beta = \gamma = 90.0°$
$\rho_{\mathrm{measd}} = 1.40 \pm 0.01$ g/cm$^{-3}$
$\rho_{\mathrm{calcd}} = 1.423 \pm 0.002$ g/cm$^{-3}$
$V = 2076.7$ Å$^3$
$\lambda$ (Mo K$\alpha$) = 0.71069 Å
$\mu$ (Mo K$\alpha$) = 7.82 cm$^{-1}$
Temperature = 25 ± 1°

| | Obsd | Acentric | Centric |
|---|---|---|---|
| $\langle E \rangle$ | 0.890 | 0.886 | 0.798 |
| $\langle E^2 \rangle$ | 0.995 | 1.000 | 1.000 |
| $\langle E^2 - 1 \rangle$ | 0.705 | 0.736 | 0.968 |

stants were determined by a least-squares fit of the diffractometer $2\theta$, $\phi$, and $\chi$ setting angles for 10 accurately centered, moderately intense reflections. The final values of the cell parameters and their estimated standard deviations are given in Table I. Assuming four formula weights of Fe $C_{18}N_8H_{24} \cdot 2H_2O$ per unit cell, the calculated density is $1.423 \pm 0.002$ g cm$^{-3}$. Because of the apparent ease with which the lattice water is lost from these crystals,[18] it is probable that the experimentally determined density was a few per cent low; the crystals used had been exposed to the atmosphere for several days prior to the density determination. The expected value for the number of water molecules per asymmetric unit is therefore two, as was confirmed by the structure analysis.

The crystal used for the data collection, a freshly grown truncated octahedron approximately 0.3 mm in diameter, was mounted on a glass fiber and encased in a thick layer of epoxy to prevent the loss of its water of crystallization.

The data were collected on a Picker FACS-1 automated diffractometer using the $\theta$–$2\theta$ scan technique with a scan rate of 1°/min. The takeoff angle was 2.0°. The scan width was varied as a function of $2\theta$ to compensate for $\alpha_1$–$\alpha_2$ splitting at high angles. The minimum scan width was 2.0° at $2\theta = 0.0$. Ten second stationary counter–stationary crystal backgrounds were measured at each end of the scans. The 117, 801, and 160 reflections were recollected after every 100 reflections as a check on the crystal condition. The data were collected first out to $2\theta = 40.0°$, then subsequently spherical shells 5° wide in $2\theta$ were collected up to a maximum $2\theta$ of 65.0°. Above $2\theta = 40.0°$ only data in the octant with $h$, $k$, and $l$ positive were collected; below $2\theta = 40.0°$, the $l$ index was allowed to also range over the negative values $-1$ and $-2$. This was done in anticipation that this additional data would aid in the determination of the absolute configuration. Graphite monochromatized Mo K$\alpha$ ($\lambda$ 0.71069 Å) was used throughout. A total of 5478 intensities was measured. The intensities of the check reflections did not vary significantly from their average values over the period of the data collection.

The multiply measured reflections were averaged (using the weighted sum of the $F_o{}^2$) after Lorentz and polarization corrections[19] were applied. The weights were calculated from the variances of the $F_o{}^2$ found using the formula

$$\mathrm{var}\,(F^2) = \frac{1}{\mathrm{Lp}}\left\{S + \frac{T_{\mathrm{S}}{}^2(B_1B_2)}{T_{\mathrm{B}}{}^2(B_1 + B_2)} + (pS)^2\right\}$$

where $S$, $B_1$, and $B_2$ are the accumulated scan and background counts, $T_{\mathrm{S}}$ and $T_{\mathrm{B}}$ are the scan and background counting times, and $p$ is a factor[20,21] here taken to be 0.02, to account for machine fluctuations and other factors which would be expected to cause variations proportional to the reflected intensity. In view of the nearly spherical shape of the crystal and the low value of $\mu r$ ($\sim$0.12), no absorption corrections were applied. The final difference Fourier showed no peaks greater than 0.4 e Å$^{-3}$ with a general background of about 0.2 e Å$^{-3}$.

**Solution and Refinement of the Structure.** The statistical distribution of the normalized structure factors (Table I) verified that the space group was acentric. Atomic form factors were taken from a tabulation by Hanson, Herman, Lea, and Skillman[22] except for that of Fe(I) which was taken from a standard source.[23] The anomalous scattering factor for iron was that given by Cromer and Liberman.[24]

The complete structure of the anion was clearly visible in a sharpened, origin-removed Patterson map in spite of the extra images due to the symmetry of the Patterson function. The position of the iron atom was unambiguously determined from peaks on the three Harker sections. Although the structure of the anion was obvious from the map, the correct octant of the coordination sphere containing the *o*-benzoquinone diimine ligand could not be assigned *a priori*. The coordination environment of the iron is nearly octahedral—one of the octahedral axes is aligned nearly parallel to the $x$ axis and the other two are nearly parallel to the [011] and [01$\bar{1}$] directions.

A Fourier map phased using coordinates for the iron and its six nearest atoms revealed the remaining atoms in the anion. Subsequent structure factor–difference Fourier calculations revealed the remaining nonhydrogen atoms and gave an initial conventional $R$ factor[25] of 0.11 using the 1100 most intense reflections. After several cycles of least-squares refinement,[26] the hydrogen atoms were located in a difference map.

Blocked matrices were used in the final least-squares refinement; the four blocks contained, respectively, the position parameters for the anion atoms, the positional parameters for the atoms of the cation and the two water molecules, the scale, secondary extinction[27] and thermal parameters for the anion, and the thermal parameters for the cation and water molecule atoms. Only cross terms between the *blocks* were neglected in the refinement. All the parameters in all four blocks were refined in each cycle; shift factors of 0.40 allowed reasonably fast convergence to the final $R$ of 0.056[28] for the 4317 nonnegative $F_o{}^2$. The final weighted $R_w$ is 0.062, and the goodness of fit is 1.24, which suggests that the estimated standard deviations of the observed intensities were on the whole about 20% too small. The final shifts in all of the parameters were less than one-fourth esd. Table II presents the final values of the refined parameters.[29]

Because misapplication of the anomalous dispersion correction can cause errors even in nonpolar acentric space groups,[30] we decided to determine the absolute configuration of the crystal used for the data collection. Refinement was carried out (on a subset

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[18] An initial attempt at data collection failed because of a precipitous decrease in the intensity of the check reflections after several days of data collection. This decrease of intensity was attributed to crystal efflorescence during a period of very low relative indoor humidity; artificially increasing the humidity in the vicinity of the crystal partially restored the lost intensity.

[19] L. V. Azaroff, *Acta Crystallogr.*, 8, 701 (1955).

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[23] "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

[24] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

[25] $R = \Sigma|F_o - F_c|/\Sigma F_o$.

[26] Initial refinement was carried out at the University of Chicago Computation Center on an IBM 7094 computer using the SORFLS structure factor–least-squares program and the ERFR2 Sly–Shomaker Fourier program. Data reduction and other service routines were coded by one of us (G. G. C.). Final refinement was performed at the California Institute of Technology using the CRYM Crystallographic Computing System operating on an IBM 370/155.

[27] A. Larson, *Acta Crystallogr.*, 23, 664 (1967), eq 3.

[28] The quantity minimized in the least squares was

$$\Sigma\frac{(F_o{}^2 - F_c{}^2)^2}{\sigma^2(F_o{}^2)}$$

$$R_w = \left\{\frac{\Sigma(F_o{}^2 - F_c{}^2)^2/\sigma^2(F_o{}^2)}{\Sigma F_o{}^4/\sigma^2(F_o{}^2)}\right\}^{1/2}$$

[29] A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number JACS-73-3869. Remit check or money order for $3.00 for photocopy or $2.00 for microfilm.

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Table II. Final Positional and Thermal Parameters (×10⁴) and Their Estimated Standard Deviations in Parentheses[a]

| ATOM | X | Y | Z | 8ETA11 | 8ETA22 | 8ETA33 | 8ETA12 | 8ETA13 | 8ETA23 |
|---|---|---|---|---|---|---|---|---|---|
| FE | 0.04324(2) | 0.18008(3) | 0.05130(3) | 19.4(1) | 38.1(2) | 32.6(2) | -1.7(4) | -1.2(4) | 2.1(5) |
| N( 1) | 0.0635(1) | 0.0734(2) | 0.1660(2) | 22(1) | 45(2) | 35(1) | -3(2) | -1(2) | 4(3) |
| N( 2) | 0.1736(1) | 0.1639(2) | 0.0424(2) | 21(1) | 40(2) | 37(1) | -11(2) | 7(2) | -6(3) |
| N( 3) | -.1692(1) | 0.1846(2) | 0.0764(2) | 25(1) | 75(2) | 70(2) | -4(3) | 1(2) | 11(4) |
| N( 4) | 0.0180(2) | -.0362(2) | -.0935(2) | 63(2) | 64(2) | 78(2) | -15(3) | -16(3) | -56(4) |
| N( 5) | 0.0437(2) | 0.3459(2) | -.1396(2) | 55(1) | 83(2) | 63(2) | -24(4) | -17(3) | 52(4) |
| N( 6) | 0.0548(2) | 0.4009(2) | 0.1922(2) | 49(1) | 82(2) | 72(2) | -14(3) | 29(3) | -53(4) |
| N( 7) | 0.3463(1) | 0.3430(2) | 0.5132(2) | 35(1) | 44(2) | 51(2) | -8(2) | 5(2) | -4(3) |
| N( 8) | 0.3263(1) | 0.3521(2) | 0.3144(2) | 26(1) | 42(2) | 50(2) | -5(2) | 6(2) | -4(3) |
| C( 1) | 0.1489(2) | 0.0353(2) | 0.1803(2) | 25(1) | 43(2) | 36(2) | -4(2) | -4(2) | -3(3) |
| C( 2) | 0.2131(2) | 0.0887(2) | 0.1077(2) | 21(1) | 42(2) | 34(2) | -1(2) | -5(2) | -13(3) |
| C( 3) | 0.3086(2) | 0.0572(2) | 0.1133(2) | 26(1) | 59(2) | 59(2) | 5(3) | 6(3) | -9(4) |
| C( 4) | 0.3351(2) | -.0202(3) | 0.1877(3) | 25(1) | 86(3) | 73(3) | 35(3) | -10(3) | -2(5) |
| C( 5) | 0.2727(2) | -.0717(3) | 0.2596(3) | 42(2) | 67(3) | 60(2) | 25(3) | -24(3) | 16(5) |
| C( 6) | 0.1822(2) | -.0454(3) | 0.2579(2) | 40(1) | 49(2) | 46(2) | -2(3) | -6(3) | 14(4) |
| C( 7) | -.0896(2) | 0.1827(2) | 0.0683(2) | 30(1) | 45(2) | 42(2) | 6(3) | -5(2) | 12(4) |
| C( 8) | 0.0254(2) | 0.0480(2) | -.0438(2) | 28(1) | 60(2) | 41(2) | 0(2) | -2(3) | 4(4) |
| C( 9) | 0.0410(2) | 0.2838(2) | -.0683(2) | 26(1) | 46(2) | 47(2) | -4(3) | -6(3) | 5(3) |
| C(10) | 0.0488(2) | 0.3191(2) | 0.1386(2) | 25(1) | 50(2) | 45(2) | 6(3) | 6(3) | -2(4) |
| C(11) | 0.2853(2) | 0.4457(3) | 0.4838(3) | 44(2) | 48(2) | 67(2) | 16(3) | 15(3) | -14(4) |
| C(12) | 0.2777(2) | 0.4547(3) | 0.3656(3) | 30(1) | 46(2) | 62(2) | 7(3) | 6(3) | -1(4) |
| C(13) | 0.3021(2) | 0.2296(3) | 0.4738(3) | 47(2) | 42(2) | 62(2) | -16(3) | 11(3) | 2(4) |
| C(14) | 0.2870(2) | 0.2376(3) | 0.3562(3) | 48(2) | 41(2) | 74(3) | -25(3) | 11(4) | -12(4) |
| C(15) | 0.4378(2) | 0.3614(3) | 0.4602(3) | 27(1) | 94(3) | 74(3) | -4(3) | -13(3) | 25(5) |
| C(16) | 0.4262(2) | 0.3569(3) | 0.3417(3) | 23(1) | 84(3) | 65(2) | 5(3) | 13(3) | 10(5) |
| C(17) | 0.3580(3) | 0.3359(4) | 0.6305(3) | 67(2) | 93(4) | 52(2) | 4(5) | -7(4) | 6(5) |
| C(18) | 0.3155(2) | 0.3590(4) | 0.1967(3) | 46(2) | 90(3) | 51(2) | -17(4) | 3(3) | -3(5) |
| O( 1) | 0.6310(2) | 0.1812(3) | 0.3429(2) | 52(1) | 128(3) | 84(2) | -54(3) | -17(3) | 66(5) |
| O( 2) | 0.0705(2) | 0.3283(3) | 0.4081(2) | 72(1) | 142(3) | 82(2) | 2(4) | 18(3) | 16(5) |

| ATOM | X | Y | Z | 8 | ATOM | X | Y | Z | 8 |
|---|---|---|---|---|---|---|---|---|---|
| H( 1) | 0.023(2) | 0.048(3) | 0.209(2) | 5.3(8) | H(15) | 0.344(2) | 0.169(2) | 0.491(2) | 3.3(6) |
| H( 2) | 0.206(1) | 0.204(2) | 0.008(2) | 2.5(6) | H(16) | 0.322(2) | 0.184(3) | 0.325(2) | 3.2(6) |
| H( 3) | 0.346(2) | 0.090(2) | 0.068(2) | 2.5(6) | H(17) | 0.226(2) | 0.242(2) | 0.341(2) | 2.7(6) |
| H( 4) | 0.389(2) | -.031(3) | 0.196(2) | 5.0(8) | H(18) | 0.472(2) | 0.304(2) | 0.476(2) | 2.5(6) |
| H( 5) | 0.294(2) | -.118(2) | 0.308(2) | 2.8(6) | H(19) | 0.473(2) | 0.442(2) | 0.480(2) | 3.6(6) |
| H( 6) | 0.144(2) | -.082(2) | 0.299(2) | 2.5(6) | H(20) | 0.458(2) | 0.282(2) | 0.312(2) | 3.0(6) |
| H( 7) | 0.395(2) | 0.280(3) | 0.652(2) | 3.3(6) | H(21) | 0.448(2) | 0.426(2) | 0.319(2) | 3.8(7) |
| H( 8) | 0.312(2) | 0.330(3) | 0.667(3) | 5.1(8) | H(22) | 0.259(2) | 0.350(3) | 0.174(2) | 5.1(8) |
| H( 9) | 0.396(3) | 0.398(4) | 0.657(3) | 7.8(9) | H(23) | 0.342(2) | 0.440(2) | 0.171(2) | 3.6(6) |
| H(10) | 0.227(2) | 0.425(3) | 0.512(2) | 4.8(8) | H(24) | 0.355(2) | 0.296(3) | 0.172(2) | 3.8(7) |
| H(11) | 0.318(2) | 0.511(2) | 0.512(2) | 3.2(6) | H(25) | 0.610(2) | 0.198(4) | 0.281(3) | 6.3(9) |
| H(12) | 0.222(2) | 0.453(3) | 0.344(3) | 4.9(8) | H(26) | 0.588(2) | 0.133(3) | 0.364(2) | 3.9(7) |
| H(13) | 0.306(2) | 0.522(2) | 0.335(2) | 2.8(6) | H(27) | 0.031(2) | 0.395(3) | 0.442(3) | 7.9(9) |
| H(14) | 0.245(2) | 0.217(3) | 0.511(2) | 4.9(8) | H(28) | 0.063(2) | 0.349(3) | 0.340(3) | 8.1(9) |

EXTINCTION PARAMETER (EXT) = 0.00000047(5)

[a] The form of the anisotropic temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{13} + 2kl\beta_{23})] \times 10^4$.

of the data and with a simplified model)[31] on both enantiomorphs; the resulting weighted $R$ factors were compared using Hamilton's test.[32,33] At convergence the original trial structure gave $R_w = 0.046$ while the enantiomorph structure gave $R_w = 0.057$. The ratio of 1.23 indicated that the original choice of configuration was correct (the alternate hypothesis could be rejected at the 99.5% level of confidence).

## Description and Discussion of the Structure

The complex anion has a basically octahedral geometry composed of a coordinated *o*-benzoquinone diimine ligand and four cyanide ligands. The oxidized *o*-phenylenediamine ligand has a localized alternating double bond system confirming the *o*-benzoquinone formulation (IV) rather than that of low-spin iron(III) spin paired with a radical ion (III).

The bond distances are presented in Figures 1 and 2 and the angles in Table III. The standard deviations[34] in the distances involving the iron are 0.003 Å, between the "heavy" atoms, 0.004 Å, and for those involving hydrogen, 0.04 Å. The standard errors in the bond angles are 0.2° except for angles involving hydrogen where the estimated errors are 2°.

Figure 1 details the coordination about the iron atom; the distortions from octahedral geometry are small. The "bite" of the *o*-benzoquinone diimine ligand is such

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(31) The 1200 most intense reflections were used, the thermal parameters of all but the iron atoms were taken to be isotropic, and only the nonhydrogen parameters were varied. This made the dual refinement rather more economical and still gave a reasonable data to parameter ratio.

(32) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(33) J. A. Ibers and W. C. Hamilton, *ibid.*, 17, 781 (1964).

(34) The standard errors were estimated from the diagonal elements of the inverse matrix from the final least-squares cycle. Although cross terms were neglected, these errors are at most 50% too small based on the observed differences between chemically equivalent bond lengths.

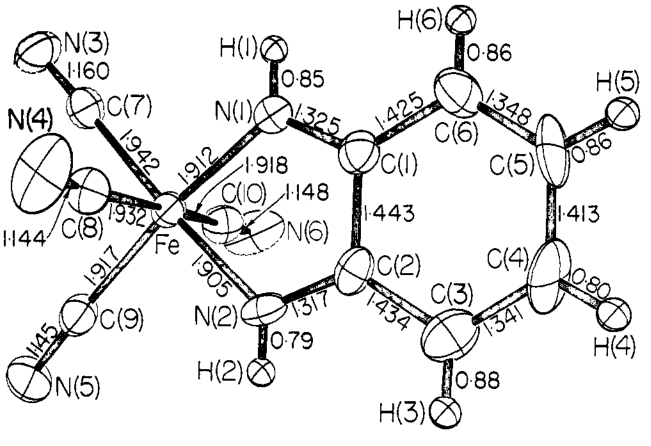


Figure 1. The atomic numbering and bond distances in the (*o*-benzoquinone diimine)tetracyanoiron(II) anion.

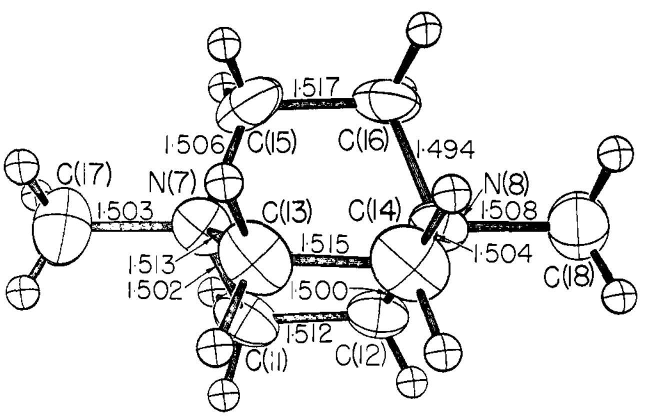


Figure 2. The atomic numbering and bond distances in the *N,N'*-dimethyl-1,4-diazabicyclo[2.2.2]octonium cation.

**Table III.** Bond Angles (deg)

| | | | |
|---|---|---|---|
| Fe–C(7)–N(3) | 178.7 | C(1)–C(2)–C(3) | 119.3 |
| Fe–C(8)–N(4) | 174.1 | C(2)–C(3)–C(4) | 118.2 |
| Fe–C(9)–N(5) | 177.1 | C(3)–C(4)–C(5) | 122.6 |
| Fe–C(10)–N(6) | 177.8 | C(4)–C(5)–C(6) | 121.7 |
| Fe–N(1)–C(1) | 116.8 | C(5)–C(6)–C(1) | 118.8 |
| Fe–N(2)–C(2) | 117.2 | C(6)–C(1)–C(2) | 119.3 |
| N(1)–Fe–N(2) | 80.4 | C(17)–N(7)–C(11) | 110.8 |
| N(1)–Fe–C(7) | 94.4 | C(17)–N(7)–C(13) | 109.4 |
| N(1)–Fe–C(8) | 91.0 | C(17)–N(7)–C(15) | 110.6 |
| N(1)–Fe–C(9) | 171.9 | C(11)–N(7)–C(13) | 108.3 |
| N(1)–Fe–C(10) | 93.6 | C(11)–N(7)–C(15) | 107.7 |
| N(2)–Fe–C(7) | 174.5 | C(13)–N(7)–C(15) | 110.0 |
| N(2)–Fe–C(8) | 91.3 | N(7)–C(11)–C(12) | 110.0 |
| N(2)–Fe–C(9) | 91.6 | N(7)–C(13)–C(14) | 109.8 |
| N(2)–Fe–C(10) | 94.0 | N(7)–C(15)–C(16) | 110.1 |
| C(7)–Fe–C(8) | 87.0 | N(8)–C(12)–C(11) | 110.2 |
| C(7)–Fe–C(9) | 93.6 | N(8)–C(14)–C(13) | 110.1 |
| C(7)–Fe–C(10) | 88.0 | N(8)–C(16)–C(15) | 109.8 |
| C(8)–Fe–C(9) | 88.1 | C(12)–N(8)–C(14) | 109.0 |
| C(8)–Fe–C(10) | 173.5 | C(12)–N(8)–C(16) | 109.2 |
| C(9)–Fe–C(10) | 88.0 | C(12)–N(8)–C(18) | 110.0 |
| N(1)–C(1)–C(2) | 112.5 | C(14)–N(8)–C(16) | 108.5 |
| N(1)–C(1)–C(6) | 128.2 | C(14)–N(8)–C(18) | 110.8 |
| N(2)–C(2)–C(1) | 112.9 | C(16)–N(8)–C(18) | 109.2 |
| N(2)–C(2)–C(3) | 127.8 | | |

that the N–Fe–N angle is compressed from 90 to 80.4°. This distortion results in the remaining ligand–Fe–ligand angles deviating from 90°; the angle between the cyanide groups trans to the *o*-benzoquinone diimine nitrogens is 93.6° and the angles between the remaining cis pairs of cyanide groups range between 87 and 88°. The coordination octahedron about the iron is symmetrically distorted. This distortion has the nature of a slight twist ($\sim$2°) down the threefold axis indicated in Figure 3. The direction of the twist is such as to decrease the C(7)–Fe–C(8), N(1)–Fe–N(2), and C(9)–Fe–C(10) angles from 90°.

The bonding in the *o*-benzoquinone diimine ligand is of particular interest. The two C–N bonds (1.321 Å) and the C(3)–C(4) and C(5)–C(6) bonds (av = 1.344 Å) are short, consistent with their identification as localized double bonds. The lengths of the four remaining C–C bonds in the ligand are intermediate between the value for a benzene C═C bond 1.392 Å, and the C—C single bond in cyclooctatetraene, 1.462 Å,[35] thus indicating that the alternating double bond structure observed here is only slightly less localized than in cyclooctatetraene.

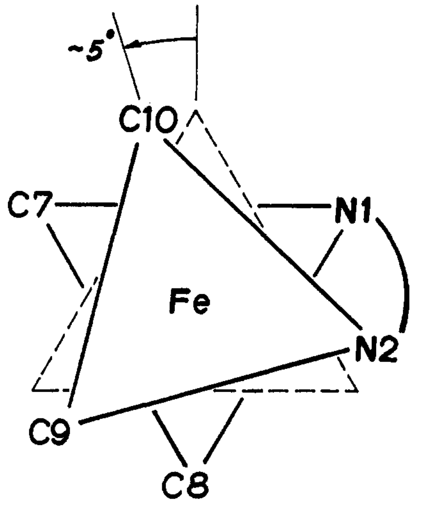


Figure 3. Schematic drawing illustrating the twisting distortion as viewed down the threefold axis of the octahedron.

The C═N and adjacent C—C bond distances for several other diimine ligands are: free dimethylglyoxime, 1.25 and 1.56 Å;[36] bis(dimethylglyoxime)platinum(II), –nickel(II), and -copper(II) complexes, 1.26 (4) and 1.54 (3) Å;[37] bis(salicylaldehyde)ethylenediiminecobalt(II) complex, 1.284 and 1.421 Å;[38] 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-dienenickel(II) perchlorate, 1.30 and 1.49 Å.[39]

If a metal ion such as low-spin Fe(II) is capable of stabilizing the α-diimine structure of *o*-benzoquinone diimine, then one would expect that metal ions, which generally stabilize Schiff base ligands, would impart substantial α-diimine character of 1,10-phenanthroline upon coordination. The average distances from 16 recently determined 1,10-phenanthroline metal complexes for the $C_{11}$–$C_{12}$ bond and for the $N_{10}$–$C_{11}$ and $N_1$–$C_{12}$ bonds are 1.42 and 1.37 Å.[40] The average length of the $N_1$–$C_2$ and $N_{10}$–$C_9$ distances is only 1.34 Å, sub-

(35) O. Bastiansen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, 27, 1311 (1957).

(36) W. C. Hamilton, *Acta Crystallogr.*, 14, 95 (1961).

(37) R. W. G. Wyckoff, "Crystal Structures," Vol. VI, Wiley, New York, N. Y., 1966, p 243.

(38) W. P. Schaefer and R. E. Marsh, *Acta Crystallogr., Sect. B*, 25, 1675 (1969).

(39) B. Y. Kilbourn, R. R. Ryan, and J. D. Dunitz, *J. Chem. Soc. A*, 2407 (1969).

(40) B. A. Frenz and J. A. Ibers, *Inorg. Chem.*, 11, 1109 (1972).

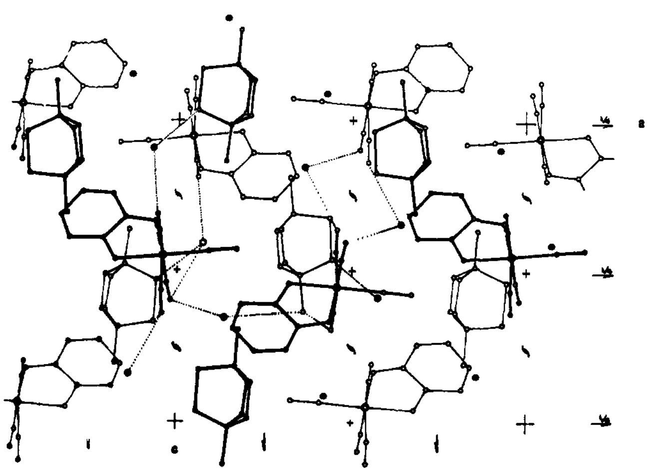
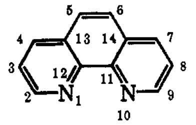


Figure 4. Packing diagram illustrating the hydrogen bonding network as viewed down the *b* axis.

stantially shorter than would be predicted from a localized alternating double bond structure as shown in V.



V

The localized $\alpha$-diimine structure is similarly lacking in complexes of $\alpha,\alpha'$-bipyridyl,[41] indicating only that the metal ion stabilization of the localized $\alpha$-diimine structure is less than the resonance stabilization energy of an extended aromatic system.

The very short iron–nitrogen distances of 1.91 Å are particularly noteworthy; they are substantially shorter than the iron–nitrogen distances, 1.97 Å, found in tris-(1,10-phenanthroline)iron(II) complexes[42] and are even slightly shorter than the average Fe–C distance for the strongly $\pi$-bonding cyanide ligands of the same moiety. The unusually short iron–nitrogen distances in this complex are indicative of the very strong binding associated with low-spin iron(II) and ligands of pure $\alpha$-diimine character such as *o*-benzoquinone diimine.

The *o*-benzoquinone diimine ligand is very nearly planar within experimental error. Packing forces appear to have rotated the ligand about the nitrogen atoms so that the iron atom is located 0.075 (8) Å on one side of the least-squares plane (defined by N(1), N(2), and C(1) through C(6). The direction cosines of the plane normal are 0.1571, 0.7540, and 0.6378.

There are two short, 1.917 and 1.918 Å, and two long, 1.932 and 1.942 Å, Fe–C bond distances in this complex. The longest is possessed by the cyano group that is not involved in any hydrogen bonds. The next longest, although hydrogen bonded to both water molecules, has its Fe–C–N angle bent nearly 6° from linear. The two remaining cyanides are both involved in hydrogen bonds. The formation of hydrogen bonds appears to bestow some degree of isocyanide character on the cyanide groups; all of the hydrogen bonded cyanides have short (av = 1.146(1) Å) C≡N bonds and shorter Fe–C distances than those of the uninvolved cyanide, C(8)≡N(4). For comparison, the average C≡N and Fe–C distances in the strongly hydrogen bonded $H_4Fe(CN)_4$ complex are 1.15(1) and 1.89(1) Å,[43] while in hexamethylisocyanoiron(II) chloride these distances are 1.15(1) and 1.85(1) Å.[44] The small deviations from linearity of the Fe–C–N angles are not unusual. Deviations of up to 9° have been documented.[45]

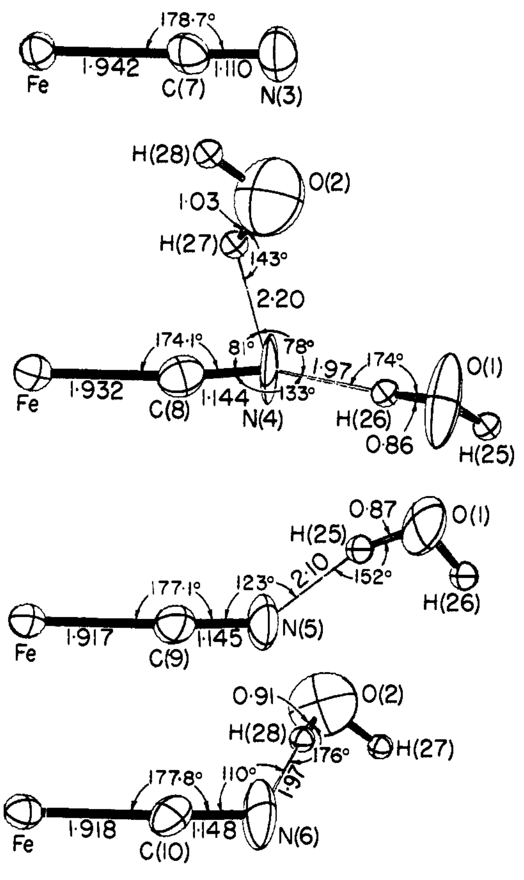


Figure 5. Details of the hydrogen bonding interactions.

Table IV. Structural Parameters for Bicyclo[2.2.2]octane Derivatives

| Compound | Bridge-head dist | C–C dist | C–C dist | Twist angle, deg | Ref |
|---|---|---|---|---|---|
| *N*-Me-Dabco | 2.595 | 1.515 | 1.493 | 0 | *a* |
| *N*-Me-Dabco H$^+$ | 2.51 | 1.53 | 1.496 | 14 | *b* |
| $Li_2$-Dabco$^{2+}$ | 2.49 | 1.56 | 1.445 | | *c* |
| *N,N'*-$Me_2$-Dabco$^{2+}$ | 2.548 | 1.515 | 1.503 | 5 | *d* |
| Bicyclo[2.2.2]octane-1,4-dicarboxylic acid | 2.597 | 1.542 | | <1 | *e* |
| Quinuclidium benzylate hydrobromide | 2.55 | 1.52 | 1.51 | 5 | *f* |
| Dabco | 2.57 | 1.57 | 1.46 | 0 | *g* |
| 1,4-Dithioniabicyclo-[2.2.2]octane$^{2+}$ | 3.13<br>(S–S) | 1.53 | 1.78<br>(C–S) | 7 | *h* |

[a] K. F. Ross and G. D. Stucky, *Inorg. Chem.*, **8**, 2734 (1969). [b] K. F. Ross and G. D, Stucky, *J. Amer. Chem. Soc.*, **92**, 4538 (1970). [c] S. P. Patterman, I. Karle, and G. D. Stucky, *ibid.*, **92**, 1150 (1970). [d] This work. [e] O. Ermer and J. D. Dunitz, *Chem. Commun.*, 567 (1968). [f] A. Meyerhoeffer and D. Carlstrom, *Acta Crystallogr., Sect. B*, **25**, 1119 (1969). [g] G. S. Weiss, A. S. Parkes, E. R. Nixon, and R. E. Hughes, *J. Chem. Phys.*, **41**, 3759 (1964). [h] E. Deutsch, private communication, 1970.

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(45) D. Britton, *Perspect. Struct. Chem.*, 1, 109 (1967).

The structure of the $Me_2$-Dabco cation is very similar to those of the parent bicyclo[2.2.2]octanes and the quinuclidinium cation. The angles about the carbon and nitrogen atoms are all close to the tetrahedral value. The average of the C–C bond distances is 1.515(2) Å and of the C–N bond distances 1.503(6) Å. Table IV lists some structural parameters for the $Me_2$-Dabco cation and several closely related compounds. Both dynamic and static disorder in the form of a small twist of one-half of the molecule relative to the other half about the threefold axis is possible in these compounds.[46] The cation in this compound is completely ordered, however, with a twist angle of 5.5° (average of the three N–C–C–N dihedral angles). Spectroscopic measurements[47] require that the twist angle be 0 ± 4°, which is consistent with the data in Table III.

The thermal motions of the atoms are generally small. They may be qualitatively evaluated from Figures 1 and 2 which were drawn using Johnson's ORTEP program.[48] None of the vibration amplitudes exceeds 0.3 Å and most are less than 0.2 Å.

The packing of the ions is shown in Figure 4, and details of the hydrogen bonds are shown in Figure 5. Neighboring anions are linked together in layers parallel to the *yz* plane by hydrogen bonds with the intervening water molecules. The average H–N distance in the hydrogen bonds is about 2 Å, about normal for an O–H···N bond. The easy loss of crystal water to the atmosphere is therefore probably due to the channels running through the lattice, as can be seen in Figure 4, which allow diffusion of the water out of the crystal.

**Acknowledgments.** We wish to thank Dr. William P. Schaefer of the California Institute of Technology for his aid with the final refinement of the structure. The support of this research by the Research Corporation and by the Advanced Research Projects Agency is gratefully acknowledged.

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(47) A. H. Nethercott and A. Javan, *J. Chem. Phys.*, 21, 363 (1953).

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# Metal Complexes as Ligands. II.[1] The Synthesis, Structure Determination, and Bonding Characteristics of Certain Tin(IV) Halide Adducts of the Nickel(II) and Palladium(II) Dithiooxalato Complexes

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*Received November 21, 1972*

**Abstract:** The synthesis of anionic complexes of the general formula $[SnX_4O_2C_2S_2MS_2C_2O_2SnX_4]^{2-}$ (where M = Ni(II) or Pd(II); X = Cl, Br, I) is described. The structure of the benzyltriphenylphosphonium salt of the bis(dithiooxalato)nickel(II) bis(stannic chloride) complex, $[(C_7H_7)(C_6H_5)_3P]_2Ni(S_2C_2O_2)_2(SnCl_4)_2$, has been determined from three dimensional X-ray data collected by counter methods. The compound crystallizes in space group $C_{2h}{}^5$-$P2_1/a$ of the monoclinic system with two molecules in a cell defined by $a$ = 14.487 (5), $b$ = 26.334 (8), $c$ = 9.912 (3) Å; $\beta$ = 124.74 (4)°. The structure has been refined by least-squares methods to a final $R$ factor on $F$ of 2.5% based on 1831 observations above background. Anions containing only a single $SnX_4$ group have also been prepared and characterized (X = Cl, F). The structure of the $[(C_7H_7)(C_6H_5)_3P]_2Ni(S_2C_2O_2)_2SnCl_4$ complex has been determined. The compound crystallizes in space group $C_{2h}{}^5$-$P2_1/c$ with four molecules in a unit cell defined by $a$ = 25.093 (15), $b$ = 15.823 (9), $c$ = 16.960 (8) Å; $\beta$ = 119.55 (6)°. The structure has been refined to a final $R$ factor on $F$ of 6.72% based on 1724 observations above background. In both structures the Ni atoms are sulfur bonded, four coordinate, and planar and the Sn atoms are octahedrally coordinated. The structure of the planar bis(dithiooxalato)nickel(II) complex, $K_2Ni(S_2C_2O_2)_2$, previously reported by Cox, *et al.*, has been refined by a three-dimensional structural analysis of X-ray data collected by counter methods. Based on 1251 observations above background a final $R$ factor on $F$ of 4.84% was obtained. Infrared spectra are reported and assigned. The Ni–S stretching frequency, previously assigned on the basis of a normal coordinate analysis, was reassigned based on isotopic substitution experiments. Differences in the vibrational spectra and the structural parameters between the $[Ni(S_2C_2O_2)_2]^{2-}$ complex and its adducts suggest coordination of $SnX_4$ groups to the already coordinated dithiooxalate ligands results in a delocalization of charge away from the nickel atoms and a strengthening of the Ni–S bond by enhanced $\pi$ back-bonding. Voltammetric studies of the adducts show reversible reduction waves. An explanation is offered for the redox properties and charge-transfer spectra of these compounds.

In recent communications[1,3,4] we have demonstrated that anionic dithiooxalate complexes can be used as ligands for coordinatively unsaturated metal complexes. In the resulting polynuclear molecules, the dithiooxalate complexes coordinate to the acceptor species either *via* the $\alpha$-diketone portion of the co-

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(1) Part I: D. Coucouvanis, *J. Amer. Chem. Soc.*, 92, 707 (1970).

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(3) D. Coucouvanis, R. E. Coffman, and D. Piltingsrud, *J. Amer. Chem. Soc.*, 92, 5004 (1970).

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