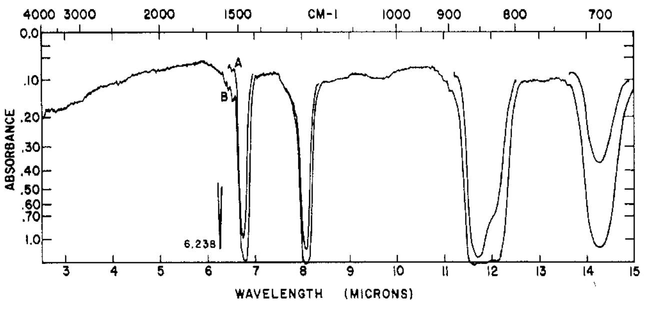

Figure 1.—Infrared spectrum of chlorine fluorosulfate: A, 8 mm; B, 30 mm.

stretching frequencies observed in alkyl hypochlorites[3a,5] and in chlorine monoxide[6] but cannot be definitely assigned.

Acknowledgment.—We wish to thank Mr. E. R. McCarthy for the mass spectral study and Mrs. R. Juurik-Hogan for analytical assistance.

[5] R. Fort, J. Favre, and L. Denivelle, *Bull. Soc. Chim. Fr.*, 543 (1955).

[6] K. Hedberg, *J. Chem. Phys.*, **19**, 509 (1951).

CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK 14850

Mössbauer Effect and Infrared Investigation of the Black Roussinate Ion [$Fe_4S_3(NO)_7^-$]

BY E. KOSTINER, J. STEGER, AND J. R. REA

Received February 9, 1970

The structure of the cesium salt of the black Roussinate ion was determined by X-ray diffraction a number of years ago.[1] The structure of the $Fe_4S_3(NO)_7^-$ ion can be described as a tetrahedral arrangement of iron atoms with sulfur atoms "bridging" three of the faces of the tetrahedron (Figure 1). The apical iron (Fe_I) is bonded to one nitrosyl group at a distance of 1.57 ± 0.04 Å while the other three iron atoms (Fe_{II}) each form bonds to two nitrosyl groups with an average Fe_{II}–N distance of 1.67 ± 0.04 Å. In addition the Fe_I atom is bonded to three sulfur atoms and forms bonds (at an average distance of 2.70 ± 0.02 Å) with the three Fe_{II} atoms and each Fe_{II} atom is bonded to two sulfur atoms and to the Fe_I atom. The average Fe_{II}–Fe_{II} distance is 3.57 ± 0.01 Å, implying no bonding interaction between these atoms.[2]

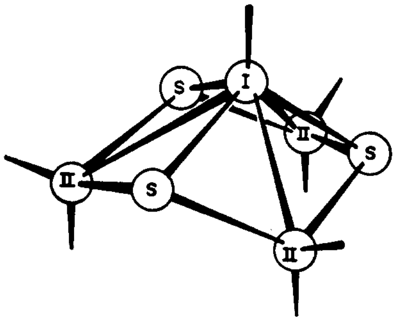

Figure 1.—The $Fe_4S_3(NO)_7^-$ ion. I is the apical iron atom; II, the other three; for clarity nitrosyl groups are indicated by a line.

Bonding in this molecular ion can be satisfactorily explained either by classical valence bond theory or by using simple molecular orbital theory.[1] The X-ray structure determination confirms the presence of two nonequivalent iron atoms: Fe_I, having C_{3v} symmetry, and Fe_{II}, having C_s symmetry, in the ratio of 1:3.

The only reported Mössbauer-effect data[3] for a Roussin's black salt (the sodium salt—the alkali metal and ammonium salts are isomorphous[1]) show the presence of a doublet characteristic of covalently bonded iron atoms (isomer shift: +0.327 mm/sec, corrected relative to sodium nitroprusside; quadrupole splitting: 0.872 mm/sec, at 25°). These data indicate that there is one type of iron atom present, in disagreement with the X-ray diffraction data. Interestingly enough, these published Mössbauer data show that the width of the resonance absorption lines (full width at half-maximum) *increases* from 0.297 to 0.360 mm/sec on lowering the temperature from 25 to −125°. Although the authors do not comment on this, it seemed suggestive that this broadening was the result of the overlap of two sets of quadrupole split peaks, the Mössbauer parameters of which displayed different temperature dependencies. It was thought that by further cooling it would become possible to resolve the data into the two sets of peaks indicated by the crystallographic investigation. Furthermore, infrared data were obtained to identify the presence (or absence) of bridging nitrosyl groups.

Experimental Section

$NH_4Fe_4S_3(NO)_7 \cdot H_2O$ was prepared from $FeSO_4 \cdot 7H_2O$ and ammoniacal H_2S according to the method of Pawel.[4] *Anal.* Calcd for $NH_4Fe_4S_3(NO)_7 \cdot H_2O$: N, 19.81; H, 1.07; S, 17.00; Fe, 39.49. Found: N, 18.99; H, 1.20; S, 16.82; Fe, 38.56.

Infrared spectra were taken in potassium bromide pellets on a Perkin-Elmer Model 521 spectrometer and in tetrahydrofuran solution on a Perkin-Elmer Model 337 spectrometer.

The iron-57 Mössbauer effect was measured with a Model NS-1 Mössbauer spectrometer (Nuclear Science and Engineering Corp., Pittsburgh, Pa.) operating in the constant-acceleration mode. The 14.4-keV γ radiation from a source of cobalt-57 diffused into palladium was detected with a gas proportional counter and collected with a 400-channel analyzer (Nuclear Chicago Corp., Chicago, Ill.) operating in time sequence scaling mode. The source and drive were calibrated against a single crystal of sodium nitroprusside (National Bureau of Standards, Standard Reference Material No. 725). The quadrupole splitting for sodium nitroprusside was taken as 1.7048 ± 0.0025 mm/sec.[5] Isomer shifts were reported with respect to the zero position of this standard. Sample thickness was 20 mg/cm² (corresponding to 8 mg of Fe/cm²). The data were reduced by a computer program which performed a nonlinear least-squares fit to the product of a series of resonant absorption peaks having

---

[1] G. Johansson and W. H. Lipscomb, *Acta Crystallogr.*, **11**, 594 (1958).

[2] Bond distances taken from ref 1.

[3] W. Kerler, *et al.*, *Z. Phys.*, **173**, 321 (1963).

[4] Reported in "Handbook of Preparative Inorganic Chemistry," Vol. 2, 2nd ed, G. Brauer, Ed., Ferdinand Enke Verlag, Stuttgart, 1962; English translation, P. G. Stecher, Ed., Academic Press, New York, N. Y., 1965.

[5] R. W. Grant, R. M. Housley, and U. Gonser, *Phys. Rev.*, **178**, 523 (1969).

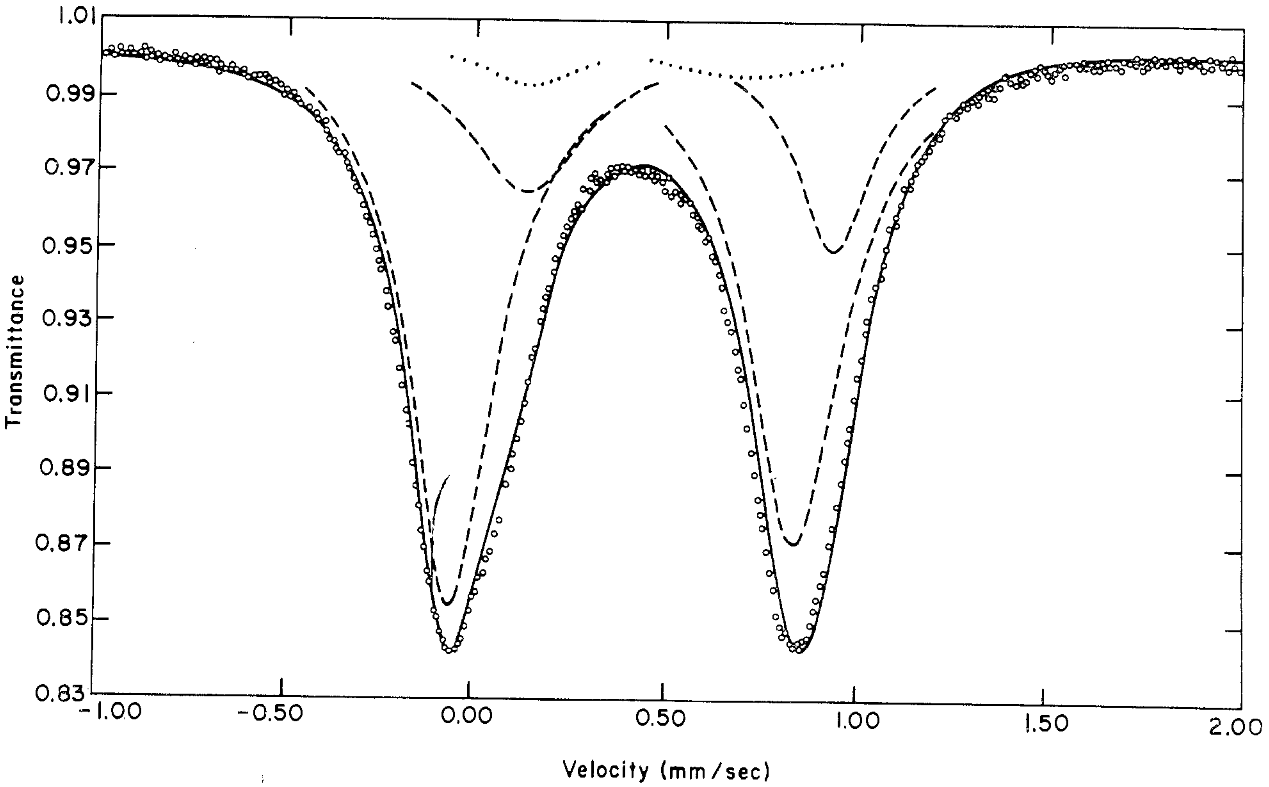

Figure 2.—Mössbauer spectrum of $NH_4Fe_4S_3(NO)_7 \cdot H_2O$. Velocity scale is relative to sodium nitroprusside: solid line, least-squares fit; dashed and dotted lines, individual peaks (see text); circles, normalized data.

Lorentzian shapes superposed on a parabolic base line, a result of our particular drive geometry. All of the variables (peak position, peak height, and peak half-width) were allowed to vary independently.

Results and Discussion

Addison and Lewis[6] first suggested a structure for the black Roussinate ion which incorporated nitrosyl groups bridging across two iron atoms. No experimental data were offered to support this proposed structure. The infrared data, however, indicate the absence of such bridging nitrosyl groups, in agreement with the X-ray crystallographic structure. Stretching frequencies for terminal nitrosyl groups bonded to iron atoms appear in the 1760-cm^{-1} region.[7] Judging from the behavior of both terminal and bridging nitrosyl groups in manganese compounds (at 1760 and 1525 cm^{-1} for stretching frequencies, respectively[8]), one should expect to find a band in the same 1500-cm^{-1} region from bridging nitrosyls. This, of course, is analogous to the well-known difference in stretching frequencies for terminal (~2000 cm^{-1}) and bridging (~1800 cm^{-1}) carbonyl moieties.

We observe a very strong band centered at 1740 cm^{-1} with shoulders at 1800 and 1710 cm^{-1} along with a medium band at 1400 cm^{-1} (attributed to the ammonium ion[9]). No absorption is observed in the 1500-cm^{-1} region.

Figure 2 illustrates the Mössbauer data collected at a sample temperature of 77°K. The solid curve is the computer fit to the experimental data (circles) and the dashed curves are the individual peaks. Note the two weak resonant peaks (dotted curves) at the center of the spectrum, due to iron in the beryllium windows of the dewar, which were prefit using data obtained without a sample and holding these parameters constant during the final least-squares fit.

We have made the assignment as follows. Numbering from left to right, peaks one and five result from one iron, peaks two and six from the other, and peaks three and four are due to the beryllium windows. The ratio of the integrated areas of peaks one and five to the areas of peaks two and six are 3.03:1, in agreement with the structure proposed on the basis of crystallographic analysis. Parameters for peaks assigned to the Roussinate ion are summarized in Table I and agree with parameters characteristic of covalently bonded low-spin iron(II).[10]

TABLE I[a]

	Isomer shift[b]	Quadrupole splitting
Fe_I	+0.522	0.802
Fe_{II}	+0.383	0.895

[a] All data in mm/sec with an error of ±0.004 mm/sec. [b] Relative to sodium nitroprusside.

The apical iron atom (Fe_I) forms bonds to three sulfur atoms, three iron atoms (at 2.70 Å), and one

---

(6) C. C. Addison and J. Lewis, *Quart. Rev., Chem. Soc.*, **9**, 115 (1955).

(7) F. Calderazzo, *et al.*, in "Organic Synthesis *via* Metal Carbonyls," Vol. 1, I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968.

(8) R. B. King, *Inorg. Chem.*, **6**, 30 (1967).

(9) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1958.

(10) J. Danon in "Chemical Applications of Mössbauer Spectroscopy," V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N. Y., 1968.

nitrosyl group while the other three iron atoms bond only to two sulfur atoms, one iron atom, and two nitrosyl groups. This effectively leads to a lower s-electron density at the Fe_I nucleus than at the Fe_{II} nucleus or, in terms of Mössbauer parameters, a more positive isomer shift. Furthermore, the d-electron back-donation from electrons on the iron atoms into the nitrosyl π orbitals would, through shielding effects, cause a lowering of s-electron density at the iron nucleus. This back-bonding is stronger in the apical iron–nitrosyl bond as indicated by both the shorter Fe–N bond and the longer N–O bond on the apical iron nitrosyl contributing to the increased isomer shift. As is to be expected from the lower symmetry of the Fe_{II} atoms, their quadrupole splitting is larger.

Both the Mössbauer and infrared data support the X-ray crystallographic strcuture for the black Roussinate ion—two different iron atoms and the presence of terminal nitrosyl groups.

Acknowledgment.—This work was supported in part by The Advanced Research Projects Agency through the Materials Science Center, Cornell University, Ithaca, N. Y. 14850.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA 32601

Synthesis and Characterization of Urea Complexes of Cobalt(III)

BY LARRY E. BENNETT

Received February 16, 1970

Hexaurea complexes of Ti(III),[1] V(III),[2] Cr(III),[3] Mn(III),[4] and Fe(III)[5] have attracted considerable spectroscopic attention. Further, the manganese complex has recently found an intriguing application as a synthetic intermediate in the nonaqueous preparation of previously unknown Mn(III) complexes containing six nitrogen donor atoms.[4] In this context we wish to report the synthesis and partial characterization of $Co[OC(NH_2)_2]_6(ClO_4)_3$, an easily handled, anhydrous, substitution-labile cobalt(III) source (desiccator life >18 months), which logically extends the Ti–Fe sequence. We also describe $(NH_3)_5Co[OC(NH_2)_2](ClO_4)_3$. These results provide compounds of potential utility as synthetic intermediates as well as further spectroscopic data on urea complexes.

Experimental Section

$Co[OC(NH_2)_2]_6(ClO_4)_3$.—Perchloric acid (70–72%) was saturated with urea (~10 ml of $HClO_4$ and ~13 g of urea), then with sodium perchlorate, and again with urea. $Co(ClO_4)_2 \cdot 6H_2O$ (6.3 g) dissolved in a minimum amount of 2 *M* $HClO_4$ (final volume ~11 ml) was electrolytically oxidized using a platinum cup, immersed in an ice bath, as both container and anode and a platinum wire as the cathode. The blue-purple solution (still containing some Co(II)) obtained after extended electrolysis was added dropwise, with stirring, to the urea–perchloric acid solution at 0°. During the Co(III) addition, additional urea and sodium perchlorate were added to maintain high concentrations. The resulting murky suspension was filtered, yielding a pinkish red filtrate and a bright green solid which was thoroughly washed with small portions of ice-cold absolute ethanol until no red color wss evident in the washings and then dried under vacuum. *Anal.* Calcd: C, 10.18; N, 23.75; H, 3.39; Co, 8.33. Found: C, 10.00; N, 23.37; H, 3.33; Co, 7.95 (by atomic absorption). Allowance for 1.2% occluded $NaClO_4$ (by atomic emission, courtesy of Mr. Ron Miller) brings these values to 10.1, 23.6, 3.37, and 8.05. After correction for nonmetal components, the "residual paramagnetism" of Co(III) is 36×10^{-6} cgsu (20°) leading to $\mu_{eff} = 0.95$ BM. Infrared absorption (excluding Nujol and perchlorate contributions) occurs at 3480 (s), 3360 (s), 3220 (sh), 1620 (s), 1527 (s), 1503 (s), 770 (w, sh), 756 (w, sh), 730 cm^{-1} (w). The compound dissolves in water with rapid loss of color and reduction to Co(II). In water saturated with urea, the low-energy visible absorption decays with $t_{1/2} \cong 50$ min (25°). Extrapolation to time of dissolution yielded λ (ϵ): 613 (30), 330 nm (340) (as poorly defined shoulder on high-energy absorption). In contrast, a Kel-F mull spectrum of the solid reveals a different absorption pattern [λ: 660, 470, ~350 nm (the last a poorly defined shoulder)].

$Co(NH_3)_5[OC(NH_2)_2](ClO_4)_3$.—$Co(NH_3)_5(H_2O)(ClO_4)_3$ (1 g) in 6 ml of urea-saturated water was stirred for 2.5 hr at 65° during which time the solution darkened considerably without appearing to change color. After storage at −10° for ~12 hr, 1 ml of 70% $HClO_4$ was added dropwise with stirring and the resulting small amount of solid was filtered off. Addition of *ca.* 20 ml of ethanol to the filtrate resulted, after 10 min of standing in an ice bath, in a precipitate which was filtered, washed with ethanol and ether, and vacuum dried to yield a pale red solid. *Anal.* Calcd: C, 2.39; H, 3.78; N, 19.53. Found: C, 2.59; H, 3.87; N, 19.55. The urea components of the infrared absorption are quite similar to those reported above for the hexaurea complex. Visible spectral data in water for this less labile complex yielded λ (ϵ): 503 (93), 345 nm (135) (a shoulder) (while generation of this complex seems assured by the described procedure, successful isolation seems dependent on poorly understood variables with acceptable product not being obtained on every attempt).

Discussion

Our infrared and magnetic measurements indicate for both cases that urea is coordinated through oxygen[3d] to an essentially diamagnetic Co(III) center. Spectral comparison with $Co(H_2O)_6^{3+}$ [$\lambda(\epsilon)$: 605 (36), 405 nm (45)[6]] and $Co(NH_3)_5H_2O^{3+}$ [$\lambda(\epsilon)$: 490 (47.0), 345 nm (44.1)[7]] suggests a lower spectrochemical position for urea relative to water on Co(III) in concert with the earlier studies.[1–5] The relatively high residual paramagnetism of Co(III) in the hexaurea compound[8] may be due to a closer approach to the spin state crossover point than for $Co(H_2O)_6^{3+}$,[8b] a veiw consistent with

---

[1] (a) H. Hartmann, H. L. Schlafer, and K. H. Hansen, *Z. Anorg. Allg. Chem.*, **289**, 40 (1957); (b) R. Dingle, *J. Chem. Phys.*, **50**, 545 (1969).

[2] (a) H. Hartmann and C. Furlani, *Z. Phys. Chem.* (Frankfurt am Main), **9**, 162 (1956); (b) R. Dingle, P. J. McCarthy, and C. J. Ballhausen, *J. Chem. Phys.*, **50**, 1957 (1969).

[3] (a) P. Pfeiffer, *Chem. Ber.*, **36**, 1927 (1903); (b) R. Dingle, *J. Chem. Phys.*, **50**, 1952 (1969); (c) C. E. Shaffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958); (d) R. B. Penland, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **79**, 1575 (1957).

[4] J. C. Summers and R. C. Stoufer, submitted for publication.

[5] (a) S. M. Holt and R. Dingle, *Acta Chem. Scand.*, **22**, 1091 (1968); (b) References 3b and 3c.

[6] G. Hargreaves and L. H. Sutcliffe, *Trans. Faraday Soc.*, **51**, 786 (1955).

[7] A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **83**, 793 (1961).

[8] (a) J. L. Kernahan and M. J. Sienko, *ibid.*, **77**, 1978 (1955); (b) H. L. Friedman, J. P. Hunt, R. A. Plane, and H. Taube, *ibid.*, **73**, 4028 (1951); suggested typical values for "low-spin" Co(III) of $(5–20) \times 10^{-6}$ cgsu.