be regarded, therefore, as either a symmetric H–O···H···O–H or an asymmetric H–O–H···O–H unit. In both cases the bridging unit is the result of a strong hydrogen bond between a hydroxo ligand of one trimer and an aquo ligand of another.

The M–O(H_3O_2) distances in structures **2–4** are considerably shorter than the M–O(H_2O) distances (see Table VIII). The shorter M–O(H_3O_2) distance is caused by the displacement of the metal atom toward the negatively charged $H_3O_2^-$ unit. As a result of this displacement, the equilateral triangles are slightly distorted. This distortion leads to isosceles triangles in **2** and **3** (as in the corresponding bromide salts reported in part 1) and to a completely asymmetric triangle in **4**.

It was suggested that $H_3O_2^-$ bridges may be a general phenomenon existing also between a pair of mononuclear metal ions such as M(H_2O)$^{n+}$ and M(OH)$^{(n-1)+}$ (part 1).[2b] Efforts are being made to obtain crystalline products of such species.

Notes

Contribution from the Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda, Naka-ku, Hiroshima 730, Japan

Interactions between Metal Chelate Electrolytes of 1,10-Phenanthroline and Nitrobenzene in Water: Crystal and Molecular Structure of the Nitrobenzene Solvate of Tris(1,10-phenanthroline)iron(II) Iodide Dihydrate

Terufumi Fujiwara, Etsuro Iwamoto, and Yuroku Yamamoto*

The nature of solute–solvent interactions of transition metal chelate electrolytes of 1,10-phenanthroline (phen) has long been of interest, especially in connection with racemization,[1] salting-in,[2] and resolution of optical isomers.[3]

A salting-in of nitrobenzene by the [Fe(phen)$_3$]$^{2+}$ ion was found to be abnormally large.[2] From the nitrobenzene-saturated aqueous solution of the chelate, we isolated the nitrobenzene solvate, [Fe(phen)$_3$]I$_2$·2H_2O·$C_6H_5NO_2$.[4] Moreover, a significant effect of a trace amount of nitrobenzene on the racemization of [Fe(phen)$_3$]$^{2+}$ in aqueous solutions[5] was observed, indicating a specific interaction between the chelate cations and nitrobenzene. On account of the bulkiness and aromaticity, the chelate cations were assumed to behave as a hydrophobic solute reinforcing the structure of water.[2,6] Thus, these results may be ascribed to the coupled action of the water structural effect and ion-dipole and/or van der Waals interactions to attract such molecules as nitrobenzene with π-electron systems. However, it is still necessary to explain the geometrical mode of the direct interaction between the attracted molecules and the chelate cations: whether this is
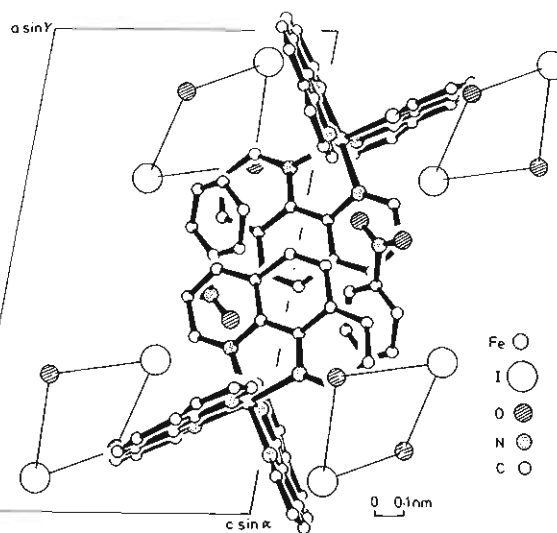

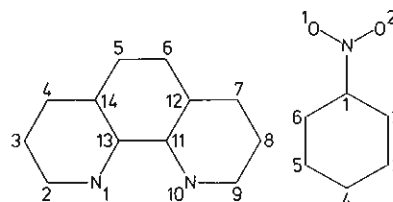**Figure 1.** Crystal packing viewed along the *b* axis.

Figure 2. Labeling scheme of the phenanthroline ligands and nitrobenzene molecules.

governed by ion-dipole or van der Waals interactions if the molecule is polar like nitrobenzene. To get information concerning the nature of the interactions involved, the crystal structure of the nitrobenzene solvate was investigated.

Experimental Section

Dark red triclinic crystals were isolated from nitrobenzene-saturated aqueous solutions of the chelate as described previously.[4] The intensities and cell dimensions were measured on a RIGAKU AFC-5 four-circle diffractometer with Mo Kα radiation (λ = 0.7107 Å) monochromated by a graphite plate at −40.0 ± 0.5 °C. The size of crystal used for the X-ray measurement was 0.30 × 0.19 × 0.21 mm^3. No systematic absence suggested the possible space group P1 or P$\bar{1}$, but the former was eliminated because the intensity statistics showed the presence of an inversion center. Crystal data: fw = 1009.4, triclinic, a = 16.917 (7) Å, b = 12.350 (6) Å, c = 10.590 (5) Å, α = 114.47 (3)°, β = 80.96 (4)°, γ = 97.55 (4)°, V = 1983 Å^3, space

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(2) Iwamoto, E.; Yamamoto, M.; Yamamoto, Y. *Inorg. Nucl. Chem. Lett.* 1974, *10*, 1069. Iwamoto, E.; Tanaka, Y.; Kimura, H.; Yamamoto, Y. *J. Solution Chem.* 1980, *9*, 841.

(3) Dwyer, F. P.; Gyarfas, E. C. *Nature (London)* 1951, *168*, 29. Iwamoto, E.; Yamamoto, M.; Yamamoto, Y. *Inorg. Nucl. Chem. Lett.* 1977, *13*, 399.

(4) Iwamoto, E.; Tarumoto, T.; Tarui, T.; Yamamoto, Y. *Chem. Lett.* 1972, 755.

(5) Iwamoto, E.; Fujiwara, T.; Yamamoto, Y. *Inorg. Chim. Acta* 1980, *43*, 95.

(6) Yamamoto, Y.; Tominaga, T.; Tagashira, S. *Inorg. Nucl. Chem. Lett.* 1975, *11*, 825.

Table I. Final Parameters for Non-Hydrogen Atoms in $[Fe(phen)_3]I_2 \cdot 2H_2O \cdot C_6H_5NO_2{}^a$

atom	x	y	z	atom	x	y	z
I(1)	0.06881 (3)	0.23682 (4)	0.22818 (6)	C(5)	0.0405 (5)	0.5354 (6)	1.1614 (7)
I(2)	0.31413 (5)	0.34380 (5)	0.57247 (7)	C(6)	−0.0075 (4)	0.6278 (6)	1.1981 (8)
Fe	0.22916 (5)	0.77948 (7)	0.92202 (9)	C(7)	−0.0262 (4)	0.8238 (6)	1.1935 (8)
O(1)[b]	0.1315 (5)	0.1618 (10)	0.4929 (11)	C(8)	0.0014 (5)	0.9107 (7)	1.1478 (8)
O(2)[b]	0.2821 (4)	0.2637 (8)	0.2118 (7)	C(9)	0.0772 (4)	0.9023 (6)	1.0658 (7)
				N(10)	0.1225 (3)	0.8113 (4)	1.0322 (5)
	phen 1			C(11)	0.0928 (4)	0.7240 (5)	1.0785 (6)
N(1)	0.3394 (3)	0.7431 (4)	0.8258 (5)	C(12)	0.0183 (4)	0.7255 (6)	1.1582 (7)
C(2)	0.3626 (5)	0.6752 (6)	0.6933 (7)	C(13)	0.1441 (4)	0.6303 (5)	1.0437 (6)
C(3)	0.4439 (5)	0.6593 (7)	0.6434 (8)	C(14)	0.1174 (4)	0.5357 (6)	1.0839 (7)
C(4)	0.5016 (5)	0.7124 (8)	0.7295 (9)				
C(5)	0.5338 (5)	0.8440 (8)	0.9738 (10)		*Nitrobenzene 1*[c]		
C(6)	0.5079 (5)	0.9167 (8)	1.1069 (9)	N	0.538 (2)	0.588 (2)	0.157 (3)
C(7)	0.3924 (5)	1.0066 (7)	1.2872 (8)	O(1)	0.540 (2)	0.480 (2)	0.104 (3)
C(8)	0.3116 (6)	1.0129 (7)	1.3178 (7)	O(2)	0.590 (2)	0.656 (2)	0.130 (3)
C(9)	0.2604 (5)	0.9461 (6)	1.2142 (7)	C(1)	0.469 (2)	0.639 (2)	0.256 (3)
N(10)	0.2877 (3)	0.8762 (5)	1.0850 (5)	C(2)	0.469 (2)	0.762 (3)	0.328 (3)
C(11)	0.3698 (4)	0.8701 (5)	1.0536 (7)	C(3)	0.399 (4)	0.808 (5)	0.412 (6)
C(12)	0.4246 (5)	0.9304 (7)	1.1506 (8)	C(4)	0.337 (2)	0.746 (3)	0.425 (4)
C(13)	0.3961 (4)	0.7973 (5)	0.9145 (7)	C(5)	0.333 (2)	0.626 (3)	0.354 (3)
C(14)	0.4792 (4)	0.7843 (7)	0.8705 (8)	C(6)	0.402 (2)	0.560 (3)	0.261 (4)
	phen 2				*Nitrobenzene 2*[c]		
N(1)	0.1791 (3)	0.6903 (5)	0.7489 (5)	N	0.552 (2)	0.769 (2)	0.281 (4)
C(2)	0.1546 (4)	0.5746 (6)	0.6892 (7)	O(1)	0.599 (2)	0.711 (3)	0.186 (3)
C(3)	0.1200 (5)	0.5238 (6)	0.5650 (7)	O(2)	0.563 (2)	0.871 (3)	0.359 (3)
C(4)	0.1085 (5)	0.5944 (7)	0.4993 (8)	C(1)	0.473 (2)	0.713 (2)	0.303 (3)
C(5)	0.1251 (6)	0.7989 (8)	0.4967 (8)	C(2)	0.412 (2)	0.776 (2)	0.388 (3)
C(6)	0.1533 (5)	0.9164 (7)	0.5576 (9)	C(3)	0.335 (2)	0.715 (2)	0.385 (3)
C(7)	0.2270 (5)	1.0764 (6)	0.7447 (8)	C(4)	0.321 (2)	0.607 (3)	0.308 (3)
C(8)	0.2589 (5)	1.1082 (6)	0.8667 (9)	C(5)	0.380 (3)	0.540 (4)	0.223 (4)
C(9)	0.2595 (5)	1.0257 (6)	0.9251 (7)	C(6)	0.460 (2)	0.590 (3)	0.218 (3)
N(10)	0.2313 (3)	0.9134 (4)	0.8642 (5)				
C(11)	0.1979 (4)	0.8813 (5)	0.7438 (6)		*Nitrobenzene 3*[c]		
C(12)	0.1925 (4)	0.9595 (6)	0.6806 (7)	N	0.453 (2)	0.865 (3)	0.454 (3)
C(13)	0.1683 (4)	0.7587 (5)	0.6803 (6)	O(1)	0.515 (2)	0.906 (2)	0.427 (3)
C(14)	0.1330 (5)	0.7168 (7)	0.5566 (7)	O(2)	0.406 (2)	0.917 (3)	0.549 (3)
				C(1)	0.429 (2)	0.737 (2)	0.361 (3)
	phen 3			C(2)	0.350 (2)	0.692 (3)	0.386 (4)
N(1)	0.2158 (3)	0.6403 (4)	0.9713 (5)	C(3)	0.334 (2)	0.567 (2)	0.302 (3)
C(2)	0.2667 (5)	0.5549 (6)	0.9388 (8)	C(4)	0.390 (2)	0.505 (3)	0.209 (3)
C(3)	0.2437 (5)	0.4557 (6)	0.9760 (9)	C(5)	0.461 (3)	0.548 (4)	0.191 (5)
C(4)	0.1714 (5)	0.4459 (6)	1.0469 (8)	C(6)	0.488 (2)	0.671 (3)	0.264 (3)

[a] Estimated standard deviations in parentheses refer to the last digit. [b] The designations "O(1)" and "O(2)" denote oxygen atoms of water molecules. [c] The atoms of these nitrobenzene molecules were allocated with a one-third occupancy.

group $P\bar{1}$, ρ(obsd) = 1.65 g·cm⁻³, ρ(calcd) = 1.69 g·cm⁻³, Z = 2. The intensity data were collected in the 2θ–ω scan mode up to 2θ = 55°. Of the 7386 unique observed reflections, 5301 reflections with $|F_o| > 3\sigma|F_o|$ were used for the structure determination. Corrections for absorption effect were neglected [μ(Mo Kα) = 20.2 cm⁻¹]. The structure was solved by the heavy-atom methods. The positions of all atoms except those of the nitrobenzene molecule were revealed from the Fourier synthesis. The electron density map showed the disordered character of the nitrobenzene molecule.[7] Several cycles of the block-diagonal least-squares refinement without the nitrobenzene molecule reduced the R value [$R = \sum(|F_o| - |F_c|)/\sum|F_o|]$ to 0.085. At this stage, a difference map was examined for the positions of the nitrobenzene molecule with reference to the calculated ones based on the reported data.[8] The best fit was attained on the basis of the following model: the molecule occupies three possible positions (in equal weight) related by about 60° rotation around the axis perpendicular to the center of the benzene ring as shown in the figure.[9] The final refinement including these atomic positions of the nitrobenzene molecules with isotropic temperature factors converged the R value to 0.054 [$R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ = 0.073].[10] The weighting scheme used was $w = (\sigma_{cs}^2 + a|F_o| + b|F_o|^2)^{-1}$, where

σ_{cs} is the standard deviation obtained from the counting statistics for each reflection; the values a and b were 0.2 and 0.0009, respectively. All the atomic scattering factors, with corrections for the anomalous dispersion ($\Delta f'$ and $\Delta f''$) of iron and iodide atoms, were taken from ref 11. All the computations were carried out by using a HITAC-M-180 computer at the Hiroshima University Information Processing Center, using the UNICS programs of The Crystallographic Society of Japan with slight modifications. Final fractional coordinates for the 74 non-hydrogen atoms in $[Fe(phen)_3]I_2 \cdot 2H_2O \cdot C_6H_5NO_2$ are listed in Table I. Tables of thermal parameters, hydrogen positions, bond distances and angles, selected least-squares planes, and observed and calculated structure factors are available as supplementary material.

Results and Discussion

Figure 1 shows that the $[Fe(phen)_3]^{2+}$ cations and nitrobenzene molecules are stacked into layers parallel to the *ab* plane. Now, we can compare the structure of the nitrobenzene solvate with that reported recently for the nitrobenzene-free compound $[Fe(phen)_3]I_2 \cdot 2H_2O$;[12] it is of interest that the composition of the former, other than the nitrobenzene molecule, is the same as that of the latter. The structure of the nitrobenzene-free compound has layers of chelate cations, and zigzag chains are formed in the layers in which two of phen

(7) Almost the same results were obtained by using data collected at ambient temperature (25 °C).
(8) Trotter, J. *Acta Crystallogr.* **1959**, *12*, 884.
(9) The figure is available as supplementary material.
(10) In the final stage of the refinement, all the hydrogen atoms of the phen ligands and the nitrobenzene molecules were fixed on the calculated positions (C–H bond lengths of 1.08 Å and idealized angles). All water hydrogen atoms were also fixed on the positions between the oxygen atom and the iodide ion with idealized O–H bond lengths of 0.97 Å.

(11) Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72–95, 149–151.
(12) Johansson, L.; Molund, M.; Oskarsson, Å. *Inorg. Chim. Acta* **1978**, *31*, 117.

ligands intruding into the major pockets of the adjacent host chelate cation are almost parallel with one of the phen ligands of the host chelate cation.[12] In the present structure, although a similar chain was observed, each benzene ring of the nitrobenzene molecule occupies one of the major pockets of the host chelate cation instead of one of the two intruding phen ligands. Figure 1 shows the nitrobenzene molecules that are in the middle position of the three positions described in Experimental Section (nitrobenzene 2 in Table I). The shortest distance between a carbon atom of the nitrobenzene ring and a carbon atom of the phen ring is 3.50 Å [C(2) in nitrobenzene 2 to C(7) in phen 1],[13] suggesting π–π interaction. Each nitro group of the nitrobenzene molecules in the three positions is directed outside the host chelate cation keeping the benzene rings in almost the same position. In addition, any hydrogen atom available for hydrogen bonding is not located around the nitro groups. This geometrical feature indicates a major role of van der Waals interaction (π–π interaction) rather than ion-dipole interaction.

The mean Fe–N distance and the mean angular geometry are identical with those found in the nitrobenzene-free compound[12] and in other compounds.[14] Equivalent bond distances and angles between ligands are similar, and they also agree well with those observed in the nitrobenzene-free compound.[12] In addition, the ligand geometry closely resembles that observed for the uncoordinated ligand,[15] and the planarity of the ligands is generally good. These results indicate that, in the present case, the Fe–N bond and bonding within the ligand appear to be little perturbed by the interaction of the nitrobenzene molecule with the ligand.

Two iodide ions and two water molecules form a distorted-tetrahedral cluster (the mean O–I–O and I–O–I angles are 69.4 and 102.6°, respectively), indicating hydrogen bonding between I⁻ and H₂O (the I–O distances are 3.57–3.64 Å). The hydrophilic clusters are located between the chelate cation layers. The clusters are situated away from the pockets of the chelate cations, and there are no water molecules associated with any specific chelate cation. In contrast to this, a water molecule associated with one specific chelate cation was reported for the nitrobenzene-free compound.[12] These results reveal that the phen chelate cation evidently prefers an interaction with nitrobenzene rather than the hydrophilic clusters, showing the hydrophobic character of the pockets and the ability of the phen ligand to attract other molecules (neutral species) with π-electron systems. Thus, it is considered that in aqueous solution the neutral nitrobenzene molecules act as ligands in outer-sphere complexes. Moreover, the interaction observed here explains why the [Fe(phen)₃]²⁺ cation strongly salts in nitrobenzene in water and why a trace amount of nitrobenzene in water influences significantly the racemization rates of [Fe(phen)₃]²⁺ and [Ni(phen)₃]²⁺, supporting the view of Van Meter and Neumann.[1] The system would provide a visualized model for investigating solvent effects due to solvation of the ligands, especially on solvent-assisted racemization of tris chelate complexes.[16] In solution the nitrobenzene molecule associated with the [Fe(phen)₃]²⁺ cation is expected to be parallel to the plane of the phen ligand, but they are not parallel in the present crystal (the angle between them is ca. 41°). This should occur by steric repulsion between the iodide ion and the nitro group of nitrobenzene [the shortest distance I(2)–O(1) in nitrobenzene 2 is ca. 3.5 Å].

Supplementary Material Available: Density difference map and listings of non-hydrogen thermal parameters, hydrogen atom positions, bond distances and angles, deviations from least-squares planes, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Inorganic Chemistry,
University of Nijmegen, Toernooiveld,
6525 ED Nijmegen, The Netherlands

Determination of Reaction Entropies for the Single Steps of Two-Electron-Transfer Processes with Small $E_1° - E_2°$ Differences: Application to $Au_9(PPh_3)_8^{3+}$ and $((bpy)_2ClRu)_2pyz^{2+}$
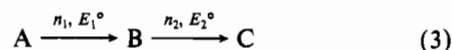
J. E. J. Schmitz and J. G. M. van der Linden*

The reaction entropy for a redox couple (eq 1) is easily determined by the measurement of the temperature coefficient of the electrode potential (eq 2) using a nonisothermal electrochemical cell.[1-4] For a two-step electron transfer (eq 3),

$$A + ne \xrightarrow{E°} B \qquad (1)$$

$$\left(\frac{dE°}{dT}\right)_{non} = \frac{dE_{1/2}}{dT} = \frac{S_B° - S_A°}{nF} = \frac{\Delta S_{AB}°}{nF} \qquad (2)$$

$$A \xrightarrow{n_1, E_1°} B \xrightarrow{n_2, E_2°} C \qquad (3)$$

the reaction entropies for the separate redox steps, $\Delta S_1°$ and $\Delta S_2°$, can also easily be obtained by this method, provided that the difference in electrode potentials is sufficiently large, i.e., when $E_1° - E_2° = \Delta E° > 250$ mV. For cases with $\Delta E°$ values < 250 mV, the current–potential curves merge and the $E°$ values are no longer directly available from the recorded voltammograms.

However, recently Richardson and Taube[5] developed a method for the determination of $E_1°$ and $E_2°$ for a two-step electrochemical charge transfer ($n_1 = n_2 = 1$), for cases where $\Delta E°$ is in the range of -200 to $+200$ mV. From the measured peak width $E_p - E_{p/2}$ or peak separation in the cyclic voltam-

(1) Yee, L. E.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131.
(2) Sahami, S.; Weaver, M. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *122*, 155, 171.
(3) It has been shown[1,2] that contributions to $(dE°/dT)_{non}$ arising from temperature gradients across the liquid junction and the working electrode are small and can also be neglected in nonaqueous solvents.[2,4]
(4) Schmitz, J. E. J.; van der Linden, J. G. M., in preparation.
(5) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.
(6) Neglectable differences are assumed to exist between $E°$ and $E_{1/2}$ for which[7]

$$E_{1/2} = E° + (RT/nF) \ln (D_{ox}^{1/2}/D_{red}^{1/2})$$

while in the cases treated here, the differences in the diffusion coefficients of the various species will be small.

(13) The numbers in parentheses correspond to those of the atoms of the phenanthroline ligands and nitrobenzene molecules (designated in Figure 2) in Table I and the supplementary material.
(14) Zalken, A.; Templeton, D. H.; Ueki, T. *Inorg. Chem.* **1973**, *12*, 1641. Baker, J.; Engelhardt, L. M.; Figgis, B. N.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1975**, 530.
(15) Smith, G.; O'Reilly, E. J.; Kennard, C. H. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1977**, 1184. Hall, S. R.; Kepert, D. L.; Raston, C. L.; White, A. H. *Aust. J. Chem.* **1977**, *30*, 1955. Thevenet, G.; Toffoli, P.; Rodier, N.; Céolin, R. *Acta Crystallogr., Sect. B* **1977**, *B33*, 2526.
(16) Kepert, D. L. *Inorg. Chem.* **1974**, *13*, 2758.