

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 compound¹² 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].

Acknowledgment. The authors thank Dr. Yoshihiko Kushi for valuable suggestions in techniques of X-ray analysis and for helpful comments. The work has been partially supported by Grant-in-Aid for Scientific Research No. 57740317 from the Ministry of Education, Science, and Culture.

Registry No. [Fe(C₁₂N₂H₈)₃]I₂·2H₂O·C₆H₅NO₂, 38703-10-5.

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 $E_1^\circ - E_2^\circ$ Differences: Application to Au₉(PPh₃)₈³⁺ and ((bpy)₂ClRu)₂pyz²⁺

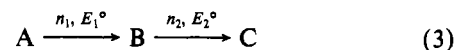
J. E. J. Schmitz and J. G. M. van der Linden*

Received May 3, 1983

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),



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



the reaction entropies for the separate redox steps, ΔS_1° and ΔS_2° , can also easily be obtained by this method, provided that the difference in electrode potentials is sufficiently large, i.e., when $E_1^\circ - E_2^\circ = \Delta E^\circ > 250$ mV. For cases with ΔE° 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 Taube⁵ 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 ΔE° 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 $(dE^\circ/dT)_{\text{non}}$ 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 which⁷

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

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.

Table I. Parameters for Cyclic Voltammetric Method^a

| temp, K | $E_p - E_{1/2}$, mV | ΔE_p , mV | $E_p - E_{p/2}$, mV | i_p ^b |
|---|----------------------|-------------------|----------------------|--------------------|
| $\Delta E^\circ = E_1^\circ - E_2^\circ = 140$ mV | | | | |
| 253 | 160.5 | 181.5 | 169.0 | 0.658 |
| 263 | 161.0 | 182.5 | 170.0 | 0.662 |
| 273 | 161.5 | 183.5 | 170.5 | 0.666 |
| 283 | 162.0 | 184.5 | 171.0 | 0.670 |
| 293 | 162.5 | 185.5 | 171.5 | 0.674 |
| 303 | 163.0 | 187.0 | 172.0 | 0.678 |
| $\Delta E^\circ = 130$ mV | | | | |
| 253 | 150.0 | 170.5 | 158.0 | 0.666 |
| 263 | 150.5 | 171.5 | 159.0 | 0.670 |
| 273 | 151.0 | 172.5 | 159.5 | 0.674 |
| 283 | 151.5 | 173.5 | 160.0 | 0.679 |
| 293 | 152.0 | 174.5 | 160.5 | 0.683 |
| 303 | 152.5 | 175.5 | 161.0 | 0.687 |
| $\Delta E^\circ = 120$ mV | | | | |
| 253 | 139.5 | 159.5 | 147.0 | 0.675 |
| 263 | 140.0 | 160.5 | 148.0 | 0.679 |
| 273 | 140.5 | 161.5 | 148.5 | 0.684 |
| 283 | 141.0 | 162.0 | 149.0 | 0.688 |
| 293 | 141.0 | 162.5 | 149.0 | 0.692 |
| 303 | 141.5 | 163.5 | 149.5 | 0.697 |
| $\Delta E^\circ = 40$ mV | | | | |
| 253 | 46.0 | 57.0 | 55.5 | 0.843 |
| 263 | 46.0 | 57.5 | 56.0 | 0.849 |
| 273 | 46.5 | 58.5 | 57.0 | 0.855 |
| 283 | 46.5 | 59.0 | 58.0 | 0.861 |
| 293 | 46.5 | 60.0 | 58.5 | 0.866 |
| 303 | 47.0 | 61.0 | 59.5 | 0.871 |
| $\Delta E^\circ = 30$ mV | | | | |
| 253 | 36.0 | 48.0 | 47.5 | 0.886 |
| 263 | 36.5 | 49.0 | 48.5 | 0.891 |
| 273 | 37.0 | 50.5 | 50.0 | 0.896 |
| 283 | 37.5 | 51.5 | 51.0 | 0.901 |
| 293 | 37.5 | 52.5 | 52.0 | 0.905 |
| 303 | 38.0 | 53.5 | 53.0 | 0.908 |
| $\Delta E^\circ = 20$ mV | | | | |
| 253 | 28.0 | 42.0 | 42.0 | 0.931 |
| 263 | 28.5 | 43.5 | 43.0 | 0.935 |
| 273 | 29.0 | 44.5 | 44.5 | 0.938 |
| 283 | 29.5 | 46.0 | 45.5 | 0.941 |
| 293 | 30.0 | 47.5 | 47.0 | 0.943 |
| 303 | 30.5 | 48.5 | 48.5 | 0.946 |

^a Peak potential ($E_p - E_{1/2}$), peak-to-peak difference (ΔE_p), and half-width ($E_p - E_{p/2}$) of a two-step cyclic wave as a function of ΔE° and temperature. ^b Peak current (i); for the definition of the peak current see ref 5.

mograms and their set of tabulated parameters, the desired half-wave potentials⁶ can be directly obtained from a simple calculation. This set of parameters is available for one temperature only (298 K). For the determination of the temperature coefficients of the standard-electrode potentials for such a two-step electron transfer, the same set of parameters

has to be calculated for every temperature of interest.

The results of our calculations for six different temperatures in the range 253–303 K and ΔE° values of interest (vide infra) are given in Table I.

Compounds exhibiting a two-electron-transfer process with small ΔE° values are the recently described gold cluster compound⁸ $\text{Au}_9(\text{PPh}_3)_8^{3+}$, undergoing a two-electron reduction with $\Delta E^\circ = 40$ mV, and the binuclear ruthenium complex⁹ $((\text{bpy})_2\text{CIRu})_2\text{pyz}^{2+}$, which can be oxidized in two steps with $\Delta E^\circ = 130$ mV.

The dependencies of E° on temperature for these two compounds were determined by cyclic voltammetry at a platinum working electrode in acetone solutions (0.1 M Bu_4NPF_6) following the Richardson-Taube procedure with use of the parameters assembled in Table I. The electrode potentials obtained in this way for six different temperatures and the entropies of the reaction derived therefrom are summarized in Table II.

From both simple electrostatic (eq 4)¹⁰ and solvent struc-

$$\Delta S^\circ_{\text{Born}} = (e^2N/\epsilon T)(d \ln \epsilon / d \ln T)((-2z + 1)/2r) \quad (4)$$

ture-making-structure-breaking concepts,¹¹ it follows that ΔS° should be positive and should decrease with decreasing absolute charge of the compounds. This is indeed observed for the successive reductions of the gold cluster; however, for the binuclear ruthenium complex both ΔS° values are the same within the experimental error.¹² This last observation strongly suggests that the identically coordinated metal ions in the ruthenium complex act as if they are two structurally independent redox centers. Meyer et al.⁹ has shown that in the mixed-valence $[2,3]^{3+}$ ion Ru(II) and Ru(III) have localized valences. It also appears now that the solvent layers around the Ru redox centers do not interfere. Consequently, the extent of the solvent layer accommodating the charge change on the Ru center is limited to only a few solvent molecules. More detailed investigations concerning multiredox-centered complexes are under way.

For the gold cluster compound, the ratio of the entropy values after corrections for changes in spin multiplicities ($\pm R \ln 2$) is $\Delta S_1^{\text{cor}}/\Delta S_2^{\text{cor}} = 20.0/11.8 = 1.69$.

According to the Born model, the reaction entropy for a reduction (eq 4) leaves the charge z as the only parameter for the ratio of ΔS° for the successive steps, as the radius $r = 10$ Å is the same for both the 3+ and 1+ cluster compounds^{13,14}. Thus, $(\Delta S_2^\circ/\Delta S_1^\circ)_{\text{Born}} = (-2z_2 + 1)/(-2z_1 + 1) = 1.66$. From the similarity of experimental and Born ratios, we conclude that the reaction entropies are completely dominated by the charge changes of the cluster, i.e., solely by Coulombic interactions with the solvent.

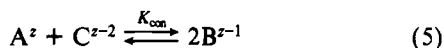
The redox center constituted by the nine gold atoms is well shielded from the solvent by the triphenylphosphine ligands, and the outer layer of the cluster is only made up of phenyl

Table II. Electrode Potentials and Reaction Entropies

| temp, K | redox couple | | | | | |
|---|---------------------------------------|------------------|------------------------------|--|------------------|------------------------------|
| | $\text{Au}_9(\text{PPh}_3)_8^{3+/2+}$ | | | $((\text{bpy})_2\text{CIRu})_2\text{pyz}^{4+/3+/2+}$ | | |
| | E_1° , mV | E_2° , mV | $E_1^\circ - E_2^\circ$, mV | E_1° , mV | E_2° , mV | $E_1^\circ - E_2^\circ$, mV |
| 253 | | | | 1149 | 1021 | 128 |
| 263 | -394 | -417 | 23 | 1163 | 1032 | 131 |
| 273 | -386 | -412 | 26 | 1175 | 1043 | 132 |
| 283 | -374 | -405 | 31 | 1182 | 1053 | 129 |
| 293 | -365 | -403 | 38 | 1192 | 1061 | 131 |
| 303 | -358 | -399 | 41 | 1198 | 1071 | 127 |
| $\Delta S_1^\circ = (dE_1^\circ/dT)F$, cal/(deg mol) | | 21.4 | | | 22.3 | |
| $\Delta S_2^\circ = (dE_2^\circ/dT)F$, cal/(deg mol) | | 10.4 | | | 22.9 | |
| $\Delta S_{\text{con}}^\circ = \Delta S_1^\circ - \Delta S_2^\circ$, cal/(deg mol) | | 11.0 | | | 0 | |
| $\Delta H_{\text{con}}^\circ = \Delta H_1^\circ - \Delta H_2^\circ$, kcal/mol | | 2.7 | | | 3.0 | |

groups. The short-range interactions between the solvent molecules and the phenyl groups are expected to undergo minor changes upon reduction and thus do not contribute to ΔS° . Furthermore, it has been argued recently⁸ that in solution only very small configurational changes occur upon reduction. Obviously, there are no contributions to ΔS° from intrinsic reorganization. In conclusion, the solvent molecules perceive only the charge changes occurring with the reduction of the cluster compound.

The thermodynamic parameters of the conproportionation equilibrium (eq 5 and 6) are closely related to those of the



$$-RT \ln K_{\text{con}} = \Delta G_{\text{con}}^\circ = \Delta H_{\text{con}}^\circ - T\Delta S_{\text{con}}^\circ = F\Delta E^\circ \quad (6)$$

successive redox steps discussed here.

It is easily seen that eq 7-9 hold, and the values found for

$$\Delta G_{\text{con}}^\circ = \Delta G_1^\circ - \Delta G_2^\circ \quad (7)$$

$$\Delta H_{\text{con}}^\circ = \Delta H_1^\circ - \Delta H_2^\circ \quad (8)$$

$$\Delta S_{\text{con}}^\circ = \Delta S_1^\circ - \Delta S_2^\circ \quad (9)$$

these parameters are also listed in Table II.

For the ruthenium compound with $\Delta S_{\text{con}}^\circ = 0$, this means $\Delta G_{\text{con}}^\circ = \Delta H_{\text{con}}^\circ = F\Delta E^\circ$, and so the driving force for the conproportionation consists only of an enthalpic term. As ΔE° is constant (Table II), the conproportionation equilibrium constant K_{con} is nearly independent from the temperature and so is the redox stability of the mixed-valence ion $((\text{bpy})_2\text{ClRu})_2\text{pyz}^{3+}$.

Experimental Section

Materials. $\text{Au}_9(\text{PPh}_3)_8(\text{PF}_6)_3$ ^{8,13} and $((\text{bpy})_2\text{ClRu})_2\text{pyz}(\text{PF}_6)_2$ ⁹ were prepared as described.

Measurements. Cyclic voltammetric measurements were made with a PAR Model 174A polarographic analyzer coupled with a PAR Model 175 universal programmer. The recording devices were a Kipp BD 30 recorder and a Tektronix 564B storage oscilloscope. No differences for ΔE_p values were noted. Sweep rates were chosen in the region for the reversible behavior of the electrode processes (100-200 mV s⁻¹). Measurements were carried out with a nonisothermal cell of the same design as that described by Weaver et al.¹ The reliability of the equipment was tested by the conduction of some pilot experiments.⁴ All measurements were made in acetone (p.a. Merck) that was 0.1 M in Bu_4NPF_6 . All potentials are referred to the Ag-AgCl (0.1 M LiCl-acetone) reference electrode. This electrode was thermostated at 20.0 °C. The working electrode was a platinum disk and the auxiliary electrode a platinum plate. The iR drop was minimized by the use of a Luggin capillary. The scan rate independency of ΔE_p for the scan rates of interest⁸ shows that no uncompensated resistance was present.

Computational Information. The cyclic voltammetric parameters were calculated with the program QUAQUA, which uses the recently introduced orthogonal collocation method.¹⁵ The program was run on a Minc 11 ED computer system. This program is able to calculate cyclic voltammograms for quasi-reversible multistep electron transfers. For the present purpose, only reversible conditions were used ($\psi = 100$). The agreement with the published values is excellent for ΔE°

(7) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods Fundamentals and Applications"; Wiley: New York, 1980.

(8) van der Linden, J. G. M.; Paulissen, M. L. H.; Schmitz, J. E. J. *J. Am. Chem. Soc.* **1983**, *105*, 1903.

(9) Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1064.

(10) $(\Delta S^\circ)_{\text{Born}}$ is derived from²

$$(-e^2N/2\epsilon T)(d \ln \epsilon / d \ln T)[(z_{\text{ox}}^2/r_{\text{ox}}) - (z_{\text{red}}^2/r_{\text{red}})]$$

with ϵ the bulk static dielectric constant and with $z_{\text{ox}} = z$ and $z_{\text{red}} = z - 1$.

(11) Abraham, M. H.; Liszi, J.; Papp, E. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 197.

> 80 mV. For $0 < \Delta E^\circ < 40$ mV, deviations of 2-3 mV were noted. A close inspection of Table II of ref 5 show some irregularities in ΔE_p for $\Delta E_{1/2} < 0$ mV.

Acknowledgment. We thank P. J. Koonen for the performance of the measurements, W. F. M. Gootzen for the writing of the computer program QUAQUA, and Professor J. J. Steggerda for his interest in this work. This investigation was supported in part by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. $\text{Au}_9(\text{PPh}_3)_8^{3+}$, 60477-23-8; $\text{Au}_9(\text{PPh}_3)_8^{2+}$, 87698-60-0; $\text{Au}_9(\text{PPh}_3)_8^+$, 84623-15-4; $[\text{Ru}(\text{bpy})_2\text{Cl}]_2\text{pyz}^{4+}$, 43225-04-3; $[\text{Ru}(\text{bpy})_2\text{Cl}]_2\text{pyz}^{3+}$, 59978-63-1; $[\text{Ru}(\text{bpy})_2\text{Cl}]_2\text{pyz}^{2+}$, 43190-72-3.

(12) For $[(\text{NH}_3)_5\text{Ru}]_2\text{pyz}^{6+/5+/4+}$ redox couples, equal entropy values were also found: $\Delta S_1^\circ = \Delta S_2^\circ = 43$ eu.

(13) Bellon, P. L.; Cariat, F.; Manassero, M.; Naldini, L.; Sansoni, M. *J. Chem. Soc. D* **1971**, 1432.

(14) van der Velden, J. W. A. Thesis, University of Nijmegen, 1982.

(15) Speiser, B.; Pons, S.; Rieker, A. *Electrochim. Acta* **1982**, *27*, 1171.

Contribution from the Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, D-6500 Mainz, FRG

Effect of Crystal Quality on the Spin-Transition Behavior in a Cobalt(II) Complex

E. W. Müller, H. Spiering, and P. Gülich*

Received January 7, 1983

Hendrickson et al.¹ have recently observed an interesting effect of crystal quality on the spin-transition behavior of an iron(III) spin-crossover complex. The change in properties is reflected in the high-spin content as a function of temperature. In particular, when the crystal quality is reduced by grinding the sample, the transition curve (magnetic moment vs temperature) flattens with increasing fractions of "residual" high-spin ions at low temperatures.

In the course of our studies on spin transitions in complexes of iron(II) we have also found that the crystal quality and history, as given by the method of preparation or by treatments of the samples such as grinding or application of pressure or γ radiation, heavily alters the spin-transition behavior.²⁻⁴

Such observations are not surprising for spin transitions of the abrupt type, where first-order phase transitions accompany the spin transition.

All spin transitions known in cobalt(II) compounds are of the gradual type, and the spin transition may extend over more than 100 K. In order to study the influence of the crystal quality, we have reexamined the spin transition in the cobalt(II) complex $[\text{Co}(\text{pmi})_3](\text{ClO}_4)_2$ (pmi = 2-pyridinal methylimine). The existence of a spin transition in $[\text{Co}(\text{pmi})_3](\text{BF}_4)_2$ has been demonstrated earlier.^{5,6} For our study,

(1) Haddad, M. S.; Federer, W. D.; Lynch, M. W.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 131.

(2) Gülich, P.; Köhler, C. P.; Köppen, H.; Müller, E. W.; Spiering, H., paper presented at the International Conference on the Applications of the Mössbauer Effect, Jaipur, India, Dec, 1981.

(3) Müller, E. W.; Spiering, H.; Gülich, P. *J. Chem. Phys.*, in press.

(4) Müller, E. W.; Spiering, H.; Gülich, P. *Chem. Phys. Lett.* **1982**, *93*, 567.

(5) Stouter, R. C.; Smith, D. W.; Cleavenger, E. A.; Norris, T. E. *Inorg. Chem.* **1966**, *5*, 1167.

(6) Schmidt, J. G.; Brey, W. S., Jr.; Stouter, R. C. *Inorg. Chem.* **1967**, *6*, 268.