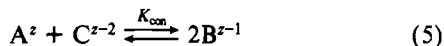


groups. The short-range interactions between the solvent molecules and the phenyl groups are expected to undergo minor changes upon reduction and thus do not contribute to ΔS° . Furthermore, it has been argued recently⁸ that in solution only very small configurational changes occur upon reduction. Obviously, 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°

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(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 $z_{\text{red}} = z - 1$.

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> 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.

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

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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,

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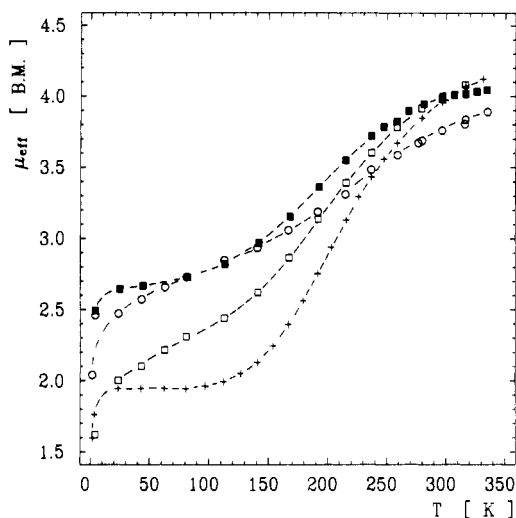


Figure 1. Effective magnetic moment of different samples of $[\text{Co}(\text{pmi})_3](\text{ClO}_4)_2$ as a function of temperature: +, preparation A from aqueous solution; \square , sample A after grinding with mortar and pestle; \blacksquare , sample A after milling for 1 h in a ball mill; \circ , preparation B from methanol solution.

however, we have chosen the perchlorate salt because it crystallizes more easily. The cobalt salt displays a spin transition similar to that of the tetrafluoroborate, if it is prepared from aqueous solution. Preparation of the salt from methanol solution leads to a chemically identical product, but the transition curve is less abrupt and the transition is incomplete (see Figure 1). To our knowledge this is the first example of a preparation effect on spin transition in cobalt(II) complexes.

Mechanical treatment of the samples alters the spin-transition curves in the present cobalt complex (see Figure 1). Even grinding with mortar and pestle, which is a relatively mild treatment, significantly flattens the transition curves; milling the samples in a ball mill (in petroleum ether suspension to avoid local heating and eventual decomposition) leads to incomplete transitions.

This behavior in cobalt(II) spin-crossover complexes completely resembles that found for iron(III)¹ and iron(II)²⁻⁴ systems, but, what is particularly surprising, in the case of the present cobalt(II) complex there is no evidence for a first-order phase transition.

This influence of mechanical treatment may be understood on the grounds of changes in the bulk elastic properties and in the strain introduced by lattice imperfections. Recently developed models for high-spin \rightleftharpoons low-spin transitions assume that a cooperative interaction is operative due to elastic deformations of the crystallites as a consequence of differences in size and/or shape of the high-spin and low-spin complex molecules.⁷⁻⁹ Therefore, a change in the elastic properties and strain in the crystal will definitely affect the spin-transition behavior in individual crystallites. Due to inhomogeneities in these changes from crystallite to crystallite, the average taken over all individual spin-transition curves of the crystallites will be "smeared out" as compared to the sharp transition of an unperturbed system. For part of the molecules, the elastic energy contributions become sufficiently large to push them out of the "spin equilibrium" into the region of stable high-spin or low-spin ground states, depending on the sign of the elastic energy contribution. This may well explain the observation of residual high-spin fractions at low temperatures and also residual low-spin fractions in the high-temperature limit.

As a consequence, in actual studies of spin-crossover systems, one has to be very careful in the quantitative interpretation of experimental data because sample preparation and sample treatment may change these such that comparison and model calculations may be meaningless.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Stiftung Volkswagenwerk for financial support.

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