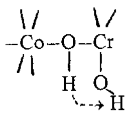
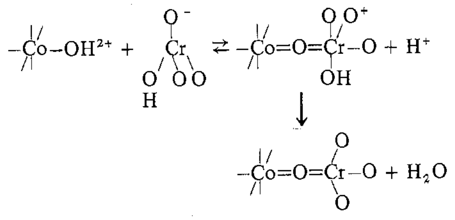


with internal proton transfer leading to water elimination. An alternative possibility is that a strong association takes place with proton elimination followed by proton-assisted water elimination

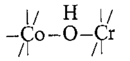


(3)

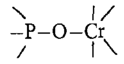
There would seem to be competition between loss of proton from the bridging oxygen, followed by rapid loss of water, and loss of water, followed by deprotonation of the bridging oxygen.

$CoOH^{2+}$ substrates differ from the other oxygen-containing substrates studied in two important respects: (1) the bridging oxygen in the active intermediate *must* be protonated and must lose the proton; (2) Co(III) has filled t_{2g} orbitals capable of donating electrons to the π system associated with the bridging oxygen.

The Co–O bond system contains filled π-antibonding orbitals which enhance its donor properties *vis a vis* Cr(VI) making the

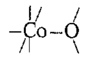


intermediate more likely to be strongly bonded than



for instance.

It must be noted that if $Co-OH_2$ is assumed the attacking ligand, $k_f = 0.8$ which compares with $k_f = 2$ for $HCrO_3^-$ of nearly identical acidity. The acid-independent term thus fits previous patterns regardless of choice of protonated form of the



ligand. The inverse acid term must, on the other hand, involve a different mechanism than either of the two paths previously recognized.

Registry No. $Co(NH_3)_5H_2O^{3+}$, 14403-82-8; $HCrO_4^-$, 15596-54-0.

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Received September 25, 1972

Diamond Cell Study of Pressure-Induced Coordination Changes for Nickel(II) in Liquid Chloride Solvents

Sir:

We wish to report some impressively simple effects of pressure on a $4 \rightleftharpoons 6$ coordination number equilibrium involving the transition metal ion Ni(II) and chloride ion ligands in a molten salt medium. The equilibrium has been investigated using a diamond anvil optical cell[1] operating under hydrostatic pressure conditions, in combination with a novel method of determining the pressure acting on the sample. Since the method is internal and allows the pressure on the sample to be defined to ±0.2 kbar at pressures up to 10 kbars, we believe we may be reporting the first really quantitative application of the diamond cell to a physicochemical problem.

The above equilibrium, which has been observed and studied in many dilute solutions of Ni(II) in molten chloride media at 1 atm pressure,[2-9] has been interpreted in terms of differences in site stabilization energies calculated from ligand field theory.[2,3] We have been concerned that the influence of the solvent, in particular the packing of the chloride ions under the influence of solvent ion forces, may not have been adequately taken into account in considering the position of the equilibrium in individual cases. This concern has motivated the present study of the effect of pressure on the state of equilibrium at constant temperature.

To simplify the experimental problem we have sought systems in which the equilibrium could be studied near room temperature, rather than at the higher temperatures common to previous, constant-pressure, studies. We achieved this by use of salts with large (weak field) organic cations for the chloride solvents. These salts also readily supercool and pass into the glassy state, a property which is vital to our pressure calibration method.

We have studied the spectrum of Ni(II) (present in $\sim$2 mol % concentrations) in two different such solvents. Both solvents are binary solutions in order to minimize the danger of solvent crystallization during the experiment. These solutions were (A) α-picolinium (α-$CH_3C_5H_4NH^+$) chloride (59.9 mol %) + ethanolaminium ($OHCH_2CH_2NH_3^+$) chloride (40.1 mol %), chosen because the $O \rightleftharpoons T$ coordination equilibrium can be shifted by change of temperature alone, and (B) α-picolinium chloride (60.5 mol %) + ethylaminium ($CH_3CH_2NH_3^+$) chloride (39.5 mol %), chosen for contrast with solvent A. Scale models (Courtold's) of the organic cations show these cations do not depart excessively from spherical symmetry; furthermore, their sizes are intermediate between those of chloride ion and the ($NiCl_4$) coordination group.

Contamination with potential ligand H_2O molecules is a problem since α-picolinium chloride is very hygroscopic. Our carefully sublimed preparation melted at 88–90° (well above the Beilstein-quoted value of 80°), and we performed all manipulations in a low dew point drybox. Our solutions nevertheless proved to contain up to 0.25 wt % (1.5 mol %) of H_2O according to Karl Fischer analysis of the stock solutions subsequent to all experiments.

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(1) L. W. Whatley, E. R. Lippincott, A. Van Valkenburg, and C. E. Weir, *Science*, 144, 968 (1964).

(2) G. P. Smith and C. R. Boston, *J. Phys. Chem.*, 62, 409 (1958).

(3) D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, 6, 23 (1963).

(4) C. A. Angell and D. M. Gruen, *J. Phys. Chem.*, 70, 1601 (1966).

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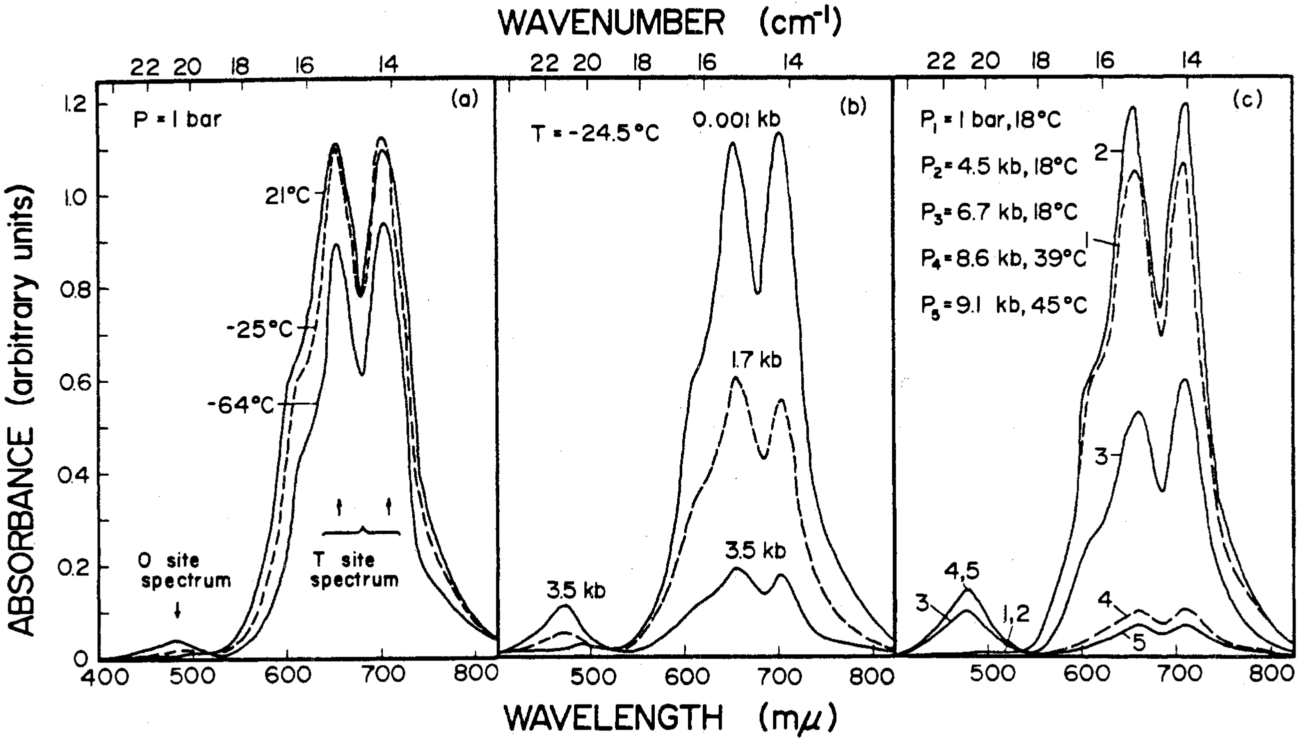

Figure 1. Effects of temperature and pressure on the spectrum of Ni(II) in liquid ionic chloride solvents: (a) solvent A (see text), temperature effect at 1 atm pressure; (b) solvent A, pressure effect at −24.5°; (c) solvent B, pressure effect at different temperatures showing "incubation" effect. Spectra under pressure were obtained on samples confined between 1 mm^2 diamond anvil windows by 0.5-mm molybdenum gaskets.

Despite the minute sample sizes ($\sim$1 $\times$ 10^{-4} cm^3) demanded by the cell, excellent spectra have been recorded, as shown in Figure 1b and c, using a Cary 14R spectrophotometer with attenuated reference beam. Spectra at 1 atm pressure were obtained using a standard 1-cm cell with an 0.97-cm spacer and are shown for the case of solvent A in Figure 1a. In solvent B the Ni(II) spectrum at 1 atm pressure is independent of temperature; only tetrahedrally coordinated Ni(II) is present from room temperature down to the glass transition temperature T_g at −56°. The spectrum is that of an almost undistorted tetrahedral species, and the molar absorptivity at 14,180 cm^{-1} is the greatest yet recorded, ϵ 210 cm^{-1} at 25° rising to 240 cm^{-1} at T_g.

Pressure calibration, which has always plagued users of the diamond cell,[10] has been achieved in a novel manner by taking advantage of the fact that all structural changes, hence spectral intensities of exchanging species, are arrested at the glass transition temperature. The glass transition, fortunately, is a pressure-sensitive phenomenon which can be accurately studied in a conventional high-pressure apparatus. Therefore, we have been able to deduce the pressure acting on a sample by observing spectroscopically the glass transition temperature, *viz.*, the temperature at which the 4 $\rightleftharpoons$ 6 equilibrium "freezes" on cooling (or "unfreezes" on warming), and then reading off the pressure from a separately determined pressure *vs.* T_g chart.[11] Since this cell pressure determination is performed internally on the solution under study, the pressure pertaining to the spectra recorded in the immediate vicinity of the glass transition can be stated confidently to within ±0.2 kbar (the error associated with determining the glass temperature).

In solvent A increase of pressure causes an immediate shift in the position of the O $\rightleftharpoons$ T equilibrium in favor of octahedral coordination, and tetrahedral sites can be eliminated completely with sufficient pressure increase. Spectra are shown in Figure 1b for the case $T = -24.5°$ and (i) $P = 3.5 \pm 0.2$ kbars (at which $T_g = -24.5°$), (ii) $P = 1$ atm, and (iii) P = some intermediate pressure estimated to be 1.7 kbars from spring compression ratios.

The presence of an isosbestic point suggests the pressure effect can be described in terms of a shift in the position of a simple two-species equilibrium. This is a much simpler type of behavior than that observed in the earlier studies of Ni(II) in high pressure-high temperature aqueous solutions by Ludemann and Franck.[12]

Using [Ni(oct)]/[Ni(tet)] concentration ratios, K_2 and K_1, determined from spectral intensities at 14,180 cm^{-1}, we obtain from the relation

$$\Delta V = -RT\frac{\ln (K_2/K_1)}{P_2 - P_1}$$

a value for the volume change accompanying the coordination change of 25 ± 5 cm^3/mol. A more recent experiment at −21° yielded $\Delta V = 26.6 \pm 1.0$ cm^3/mol. For comparison, the volume of 1 mol of spheres of radius $r_{\mathrm{Ni(II)}} + 2r_{\mathrm{Cl}^-}$ is 204 cm^3 while the volume of 2 mol of free chloride ions is 29.2 cm^3; *i.e.*, the value of ΔV is reasonable.

For solvent B, in which no octahedrally coordinated Ni(II) can be observed at 1 atm, application of pressure also produced O sites, but only after an "incubation" pressure estimated at $\sim$5 kbars had been applied. Evidently, there exists a distribution of sites of different compressibility which are eliminated progressively before T sites ($NiCl_4$) are affected (Figure 1c). An experiment in which both Ni(II) and, *e.g.*, Co(II) are present in the same solvent would be of

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(10) R. A. Forman, G. J. Piermarini, J. D. Barnett, and S. Block, *Science*, 176, 284 (1972), and references cited therein.

(11) E. Williams and C. A. Angell, data on pressure dependence of T_g obtained by high-pressure dta studies, to be published.

(12) H. D. Ludemann and E. U. Franck, *Ber. Bunsenges. Phys. Chem.*, 71, 455 (1967); 72, 514 (1968).

interest in this connection. Note, in Figure 1c, that the glass temperature has been raised a total of 101° above its 1-atm value of −56°. Extrapolation of our independently determined linear T_g *vs.* pressure plot[11] suggests a pressure of 9.1 kbars was reached in this experiment.

The octahedral band, which occurs at identical frequencies (21,000 cm^{-1}) in each solvent, is believed to be due to the $(NiCl_6)$ group. The frequency at band maximum is consistent with those of spectral bands attributed to $(NiCl_6)$ groups in previous studies[3,4,7] and, if anything falls at lower frequencies than found for Ni in octahedral sites, in other anhydrous chloride glasses[13] and in chloride crystal lattices.[3] Furthermore, (a) analysis of the temperature dependence of the $O \rightleftharpoons T$ equilibrium yields $\Delta H = 9.3 \pm 1.5$ kcal/mol, in fair accord with the value 8.5 kcal/mol found previously[5] for the all-chloride ligand coordination change and (b) wet samples (loaded outside the drybox) yielded a second higher frequency octahedral band at low temperatures. Nevertheless, the possibility of oxygen coordination from back-entering cations in solvent A and from the unexpurgated water (almost 1 H_2O per Ni(II) in solvent B) cannot be finally excluded at this point.

Without $(\partial P/\partial T)_V$ data for this solvent we cannot say to what extent the temperature-induced coordination change would be eliminated under constant- volume conditions (although for $(\partial P/\partial T)_V \approx 35$ bars deg^{-1}, a not unreasonable value, data in Figure 1a and b suggest no change at all would occur). However, it is interesting and important to realize that the coordination change now frequently observed to occur with increasing temperature in a variety of chloride solutions[4-7] is in a sense tied to the thermal expansion of the solvent. Evidently, without the solvent volume change, much less extensive coordination change would be permitted. Two questions then arise: (i) would not the value of ΔH observed for the equilibrium be expected to vary with the expansion coefficient, or internal pressure, of the solvent in which the equilibrium is observed and (ii) why is the value of ΔH observed in this and previous work at 1 atm pressure[4] in approximate agreement with the value of 10.2 kcal/mol for the octahedral site preference energy calculated by Papatheodorou[14] from recent spectral data on crystalline compounds of Ni(II)[15,16] and substantiated by appropriate heat of solution measurements?[14] Presumably, the answer to the latter question is that the crystal measurements all refer to 1 atm pressure, and the distance parameters used in the theoretical calculations are taken from such crystals. The former question and its relation to the somewhat similar problem of free volume *vs.* enthalpy or entropy interpretations of mass transport in viscous liquids[17] will be taken up in a later publication when $(\partial P/\partial T)_V$ data have been obtained for these and other solvents.

Registry No. Nickel, 7440-02-0; α-picolinium chloride, 14401-91-3; ethanolaminium chloride, 2002-24-6; ethylaminium chloride, 557-66-4.

Acknowledgments. The authors acknowledge support of this work by the AEC (Contract AT(11-1)-2008) and NSF (GP 30722). We are grateful to Drs. G. Papatheodorou and N. Muller for some profitable discussions of these results.

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[13] C. A. Angell, umpublished work.

[14] G. N. Papatheodorou, *J. Inorg. Nucl. Chem.*, in press.

[15] C. R. Boston, J. Brynestad, and G. P. Smith, *J. Chem. Phys.*, 47, 3193 (1967).

[16] T. W. Couch and G. P. Smith, *J. Chem. Phys.*, 53, 1336 (1970).

[17] (a) M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, 31, 1164 (1959); (b) G. Adam and J. H. Gibbs, *ibid.*, 43, 1852 (1965); (c) M. Goldstein, *ibid.*, 39, 3369 (1963).

Additions and Corrections*

1972, Volume 11

T. Herskovitz, C. E. Forbes, and R. H. Holm: Dithiotropolonates. III. Ring-Alkylation Reactions of Bis(dithiotropolonato)nickel(II) and -zinc(II) Complexes.

Page 1320. In Table I the entries under the column $E_{1/2}$, V, $-2 \rightleftharpoons -1$, should read −1.38 for Ni(Me-SST)$_2$ and −1.25 for Ni(SST)$_2$. Under the column $E_{1/2}$, V, $-1 \rightleftharpoons 0$, the entries should read −0.99 for Ni(Me-SST)$_2$ and −0.86 for Ni(SST)$_2$.—R. H. HOLM.

C. T. Goetschel, V. A. Campanile, R. M. Curtis, K. R. Loos, C. D. Wagner and J. N. Wilson: Preparation and Properties of Perfluoroammonium Tetrafluoroborate, $NF_4{}^+BF_4{}^-$, and Possible Synthesis of Nitrogen Pentafluoride.

Page 1696. Subsequent to publication of the article cited above, in which NF_4BF_4 was described as a purportedly new compound, I was informed by Dr. V. Ya Rosopovskii, Moscow, that preparation of the same compound in quite high purity had been described previously [S. M. Sinepniikov and V. Ya Rosopovskii, *Dokl. Akad. Nauk SSSR*, 194 (6), 1341 (1970)]. The properties of the compound disclosed therein are in general agreement with those described by us except for minor differences. The higher reactivity of their preparation with organic liquids may have been due to dioxygenyl tetrafluoroborate as a minor component.

We regret that we were unaware of this work at the time of our publication.—J. NORTON WILSON.

Gary E. Glass and Robert West: Formation of Chlorine Dioxide by the Electrolytic Oxidation of Perchlorate Anion.

Page 2847. In the publication of this note (reporting work carried out in 1969) we overlooked a paper by G. Cauquis and D. Serve, *J. Electroanal. Chem.*, 27 (1970) App. 3-6. In this paper the radical produced by electrochemical oxidation of perchlorate was identified as ClO_2, in agreement with our findings.—ROBERT WEST.

Doreen A. Brisbin and Geoffrey D. Richards: Kinetics of the Reaction of Some First-Row Transition Metals with Protoporphyrin IX Dimethyl Ester.

Page 2849. The equation in the ninth line of the **Treatment of the data** section should read $k_{1/2} = 2.303m/[M]^{1/2}$.—D. A. BRISBIN.

1973, Volume 12

R. G. Little and Robert J. Doedens: Crystal and Molecular Structure of Dichlorobis(nitrosobenzene)palladium(II), a Nitrogen-Bonded Arylnitrosometal Complex.

Page 537. (In abstract and in body of paper). The unit cell angle β should be 94.32 (1)°. The correct value was used in all computations of the structure analysis.—R. J. DOEDENS.

* Further Additions and Corrections will appear in the July issue.