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.

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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.