Ferrous Trisbipyridyl Chloride and Azide

$Fe(bipy)_3Cl_2 \cdot 5H_2O$ and $Fe(bipy)_3(N_3)_2 \cdot 5H_2O$ are low-spin compounds at room temperature and 1 atm. Under pressure one observes a low- to high-spin ground state change in both compounds. A comparison of the conversion from the low-spin state with pressure at 298°K for these trisbipyridyl compounds and conversion of a typical low-spin trisphenanthroline compound is presented in Fig. 21. The low-spin ferrous species in the trisbipyridyl chloride decreases from 88% at 40 kbar to about 79% at 150 kbar. The trisbipyridyl azide exhibits a nearly constant amount of low-spin species (86%–87%) over the range of 60–150 kbar. In general, the trisbipyridyl compounds exhibit less low-spin to high-spin conversion (Fig. 21) than the trisphenanthroline compounds.

Ferrous Bisbipyridyl Oxalate

Ferrous bisbipyridyl oxalate, $Fe(bipy)_2(C_2O_4) \cdot 3H_2O$, is an intermediate-spin compound according to magnetic measurements made by König and Madeja.[9] It is analogous to the bisphenanthroline oxalate discussed previously. A change from an intermediate-spin ground state to one of high spin is reflected in Fig. 22 which presents 298°K and 383°K isotherms for the bisbipyridyl oxalate. The higher conversion with pressure to the high-spin state expected for an intermediate-spin compound is observed. Also the thermal enhancement of the high-spin state at elevated temperature is again observed. The amount of conversion from the intermediate-spin ground state to a high-spin ground state is less for the bipyridyl oxalate than for the phenanthroline oxalate for corresponding isotherms, as is shown in Fig. 22.

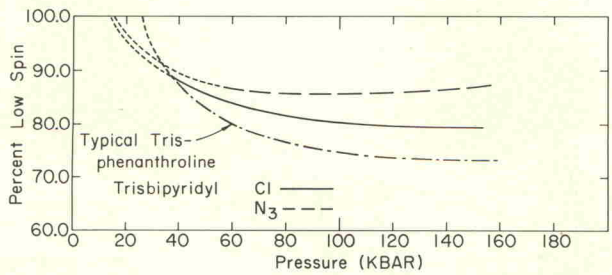

FIG. 21. Percent low-spin Fe(II) vs pressure, trisbipyridyl chloride and azide.

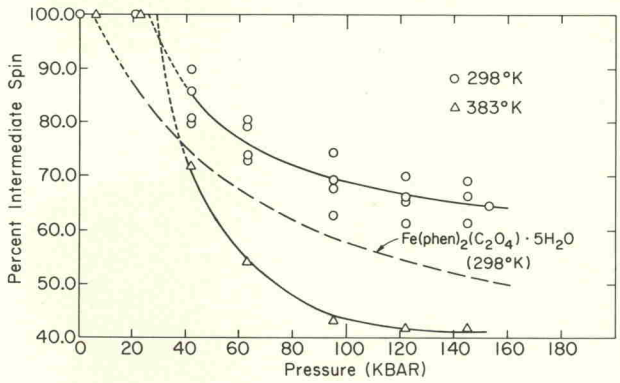

FIG. 22. Percent intermediate-spin Fe(II) vs pressure, $Fe(bipy)_2(C_2O_4) \cdot 3H_2O$.

* This work was supported in part by the U.S. Atomic Energy Commission under Contract COO-1198.

[1] E. König, Coord. Chem. Rev. **3,** 471 (1968).
[2] S. Mason, Inorg. Chim. Acta Rev. **2,** 89 (1968).
[3] P. Day and N. Sanders, J. Chem Soc. **1967,** A1530, A1536.
[4] H. G. Drickamer, Solid State Phys. **17,** 1 (1965).
[5] H. G. Drickamer and J. Zahner, Advan. Chem. Phys. **4,** 161 (1962).
[6] C. K. Jorgensen, *Absorption Spectra and Chemical Bonding in Complexes* (Pergamon, Oxford, 1962).
[7] C. B. Bargeron, M. Avinor, and H. G. Drickamer, Inorg. Chem. (to be published).
[8] K. Madeja, W. Wilke, and S. Schmidt, Z. Anorg. Allgem. Chem. **346,** 206 (1966).
[9] E. König and K. Madeja, Inorg. Chem. **7,** 1848 (1968).
[10] A. Schilt, J. Am. Chem. Soc. **82,** 3000 (1960).
[11] J. E. Fergusson and G. M. Harris, J. Chem. Soc. **1966,** A1293.
[12] P. de Brunner. R. W. Vaughan, A. R. Champion, J. Cohen, J. Moyzis, and H. G. Drickamer, Rev. Sci. Instr. **37,** 1310 (1966).
[13] R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer, J. Opt. Soc. Am. **47,** 1015 (1957).
[14] H. G. Drickamer and A. S. Balchan, in *Modern Very High Pressure Techniques*, edited by R. H. Wentorf, Jr. (Butterworths, London, 1962), pp. 25–50.
[15] A. R. Champion, R. W. Vaughan, and H. G. Drickamer, J. Chem. Phys. **47,** 2583 (1967).
[16] H. G. Drickamer, R. W. Vaughan, and A. R. Champion, Accounts Chem. Res. **2,** 40 (1969).
[17] E. Konig and K. Madeja, Inorg. Chem. **6,** 48 (1967).
[18] H. G. Drickamer, V. C. Bastron, D. C. Fisher, and D. C. Brenoble, J. Solid State Chem. **2,** 94 (1970).
[19] S. C. Fung and H. G. Drickamer, J. Chem. Phys. **51,** 5453, 4360 (1969).