

Ferrous Trisbipyridyl Chloride and Azide

$\text{Fe}(\text{bipy})_3\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{bipy})_3(\text{N}_3)_2 \cdot 5\text{H}_2\text{O}$ 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, $\text{Fe}(\text{bipy})_2(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$, 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

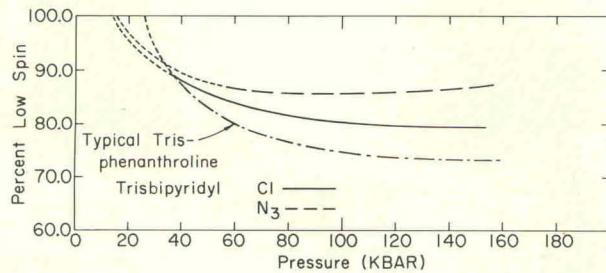


FIG. 21. Percent low-spin Fe(II) vs pressure, trisbipyridyl chloride and azide.

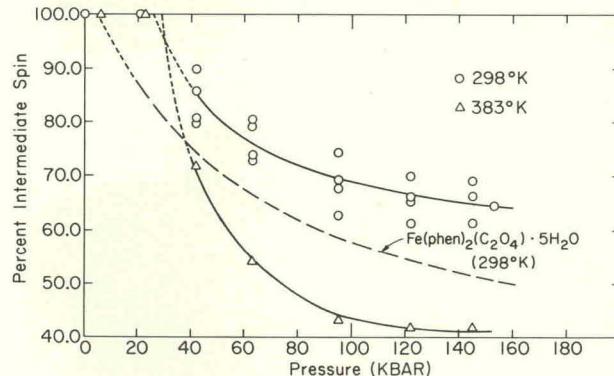


FIG. 22. Percent intermediate-spin Fe(II) vs pressure, $\text{Fe}(\text{bipy})_2(\text{C}_2\text{O}_4) \cdot 3\text{H}_2\text{O}$.

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.

* 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. Ferguson 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. Slyhouse, 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. König 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).