

# Sequence of the Lowest Excited States in Ru(phen)<sub>3</sub><sup>2+</sup> Ions

M. Král

Department of Analytical Chemistry, Institute of Chemical Technology, 166 28 Prague, Czechoslovakia

In the last ten years experimental and theoretical studies of the tris(bisbidentate) complexes where the ligands are conjugated  $\pi$ -electron molecules (e.g., 1,10-phenanthroline, 2,2'-bipyridyl) have attracted the attention of spectroscopists and theoretical chemists [1]. The spectral properties of these compounds in the region of electron-transfer transitions have attracted especial interest since there are differences in the CD spectra and also in the luminescence properties, as for example between the complexes of (–)-Fe(phen)<sub>3</sub><sup>2+</sup> and (–)-Ru(phen)<sub>3</sub><sup>2+</sup>. To explain these differences the couple-chromophore model was used to describe the electronic states of these complexes. According to this picture, the triply degenerate metal-to-ligand electron-transfer excited states split into the states A<sub>2</sub> and E [2]. The position of these states depends on the interaction which is operative in the relevant molecule. If the dipole-dipole interaction between the chromophores is the dominant factor, the <sup>1</sup>A<sub>1</sub>→<sup>1</sup>A<sub>2</sub> transition will be placed at higher energy and the <sup>1</sup>A<sub>1</sub>→<sup>1</sup>E transition at correspondingly lower energy. If, however, the other interaction (e.g., spin-orbit, vibronic or Jahn-Teller effect) should be more important than the dipole-dipole term, the level order could reverse.

We calculated the dipole-dipole interaction energy [3] for the iron(II) and ruthenium(II) complexes with 1,10-phenanthroline and the first case yielded a value of 1826 cm<sup>-1</sup> and the second case a value of 110 cm<sup>-1</sup>. (The necessary transition moments of the electron-transfer transitions were calculated using the expressions given by the semiclassical time-dependent perturbation theory [4, 5].) Another interaction which takes place in these compounds is the spin-orbit coupling scrambling the <sup>3</sup>A<sub>2</sub> and <sup>1</sup>E states [6]. The energy corresponding to this effect is 166 cm<sup>-1</sup> for the Fe(phen)<sub>3</sub><sup>2+</sup> complex and 408 cm<sup>-1</sup> for the Ru(phen)<sub>3</sub><sup>2+</sup> complex. Comparing the values of the spin-orbit coupling energy with the dipole-dipole interaction energy shows that in the case of

ruthenium(II) complex the spin-orbit coupling mechanism is operative prior to the dipole-dipole interaction which leads to the following sequence of the lowest electron-transfer states: <sup>3</sup>A<sub>2</sub> < <sup>1</sup>A<sub>2</sub> < <sup>1</sup>E [7]. This is in agreement with the results of Crosby and co-workers [8, 9], who studied experimentally the luminescence properties of these compounds and found the <sup>1</sup>A<sub>2</sub> state to be lower than the state <sup>1</sup>E. Furthermore, the shape of the CD spectra of (–)-Ru(phen)<sub>3</sub><sup>2+</sup> in the region of electron-transfer transitions agrees with this level order [10], i.e., the negative short-wave component of the CD curve of the (–)-Ru(phen)<sub>3</sub><sup>2+</sup> ion belongs to the transition

<sup>1</sup>A<sub>1</sub>→<sup>1</sup>E while its positive long-wave component belongs to the transition <sup>1</sup>A<sub>1</sub>→<sup>1</sup>A<sub>2</sub>. The same conclusion holds for the complexes of Os(II) with 2,2'-bipyridyl and 1,10-phenanthroline.

Received July 23 and September 12, 1979

1. Crosby, G.A.: Acc. Chem. Res. 8, 231 (1975)
2. Ballhausen, C.J., Gray, H.B.: Coordination Chemistry, Vol. I, p. 74 (Martell, A.E., ed.). New York: Van Nostrand 1971
3. London, F.: Trans. Faraday Soc. 33, 8 (1937)
4. Moscowitz, A.: Thesis, Harvard Univ. 1957
5. Moffitt, W.: J. Chem. Phys. 25, 467 (1956)
6. Král, M.: Theor. Chim. Acta 43, 273 (1977)
7. Král, M.: in preparation
8. Crosby, G.A., Harrigan, R.W.: J. Chem. Phys. 59, 3468 (1973)
9. Baker, D.C., Crosby, G.A.: Chem. Phys. 4, 428 (1974)
10. Král, M.: Theor. Chim. Acta 50, 355 (1979)

## Kristallstruktur von Fe<sub>3</sub>Ge<sub>2</sub>O<sub>8</sub>

Ein neues Eisen(II,III)-germanat mit kubisch-dichtester Sauerstoff-Packung

K. Kato, E. Takayama und N. Kimizuka

Mukizaishitsu Kenkyusho (National Institute for Researches in Inorganic Materials), 300–31 Ibaraki-ken, Japan

Nach vorläufigen Untersuchungen [1] über die Phasengleichgewichte existiert im System FeO-Fe<sub>2</sub>O<sub>3</sub>-GeO<sub>2</sub> eine bisher unbekannt Verbindung mit der wahrscheinlichen Zusammensetzung Fe<sub>3</sub>Ge<sub>2</sub>O<sub>8</sub>. Die röntgenographische Strukturbestimmung ergab einen neuen Strukturtyp mit kubisch-dichtester Sauerstoff-Packung. Die analoge Verbindung ist im entsprechenden Silicat-System unter normalem Atmosphärendruck nicht vorhanden [2], ihre dicht gepackte Struktur legt jedoch die Möglichkeit nahe, daß sie als Hochdruckphase auftritt.

Fe<sub>3</sub>Ge<sub>2</sub>O<sub>8</sub> kristallisiert in der Raumgruppe P2<sub>1</sub>/c mit den Gitterkonstanten a=8,479(9), b=8,333(3), c=9,196(15) Å und β=117,7(1)°; die Dichten betragen D<sub>m</sub>=5,04(5), D<sub>x</sub>=5,09 Mg m<sup>-3</sup> (Z=4). Die Struktur wurde durch Trial-and-error-Verfahren ermittelt und mit der Methode der kleinsten Quadrate verfeinert. Der R- und der wR-Wert betragen 0,049 und 0,032

für 3191 Symmetrie-unabhängige, von Null verschiedene Strukturamplituden, die mit einem Einkristalldiffraktometer im Be-

Tabelle 1. Lageparameter für Fe<sub>3</sub>Ge<sub>2</sub>O<sub>8</sub> (Standardabweichungen in Klammern; auf die Wiedergabe der anisotropen Temperaturfaktoren wird aus Platzgründen verzichtet)

Atom	x	y	z
Ge(1)	0,21997(7)	-0,02015(6)	0,23251(6)
Ge(2)	0,37151(6)	0,25205(6)	0,48828(6)
Fe(1)	0,07050(8)	0,35719(8)	0,10726(8)
Fe(2)	0,34279(8)	0,61620(8)	0,13650(8)
Fe(3)	0,19491(8)	0,61646(8)	0,37334(8)
O(1)	0,0490(4)	0,1234(4)	0,1333(4)
O(2)	0,0881(4)	0,5987(4)	0,1275(4)
O(3)	0,2967(4)	0,3682(4)	0,0979(4)
O(4)	0,2957(4)	0,8710(4)	0,1142(4)
O(5)	0,2025(4)	0,3817(4)	0,3594(4)
O(6)	0,1729(4)	0,8599(4)	0,3700(4)
O(7)	0,4094(4)	0,1104(4)	0,3615(4)
O(8)	0,4323(4)	0,6508(4)	0,3809(4)