INVESTIGATION OF MAGNETIC PROPERTIES OF A FAMILY OF MOLECULAR SQUARES BY HFEPR

F. Karadas, M. Shatruk, K.R. Dunbar (Texas A&M U., Chemistry); J. Krzystek, A. Ozarowski, D. Smirnov (NHMFL), J. Telser (Roosevelt U., Chemistry)

Introduction

The research in the field of cyanide-bridged transition metal clusters carried out in the Dunbar group resulted in the preparation of series of molecular squares of general formula $\{[Co(triphos)(CN)_2]_2[MCl_2]_2\}$ (M = Mn(II), Fe(II), Co(II), Ni(II), Zn(II)) which, in this report, are denoted as **[CoM]**. Preliminary magnetic studies demonstrated that these clusters have integer spin ground states with appreciable axial anisotropy defined by the zero-field splitting parameter *D*, which renders them EPR silent when studied by traditional X-band EPR spectroscopy (the exception being **[CoZn]**). Therefore, the study reported here was aimed at determining accurate magnetic parameters of the square clusters by means of high-frequency and -field EPR (HFEPR) and comparing the obtained values to those derived from conventional magnetic measurements using a SQUID magnetometer.

Experimental

Both the Millimeter and Sub-mm Wave Spectroscopy Facility with the 25-Tesla resistive "Keck" magnet, and the EMR Facility with a 17-Tesla superconducting magnet were employed. Experiments were performed on polycrystalline samples.

Results and Discussion

Both magnetic, and EPR studies proved that there is no magnetic exchange in the **[CoZn]** cluster, where the low-spin (S = 1/2) Co(II) ions are separated by diamagnetic Zn(II) ions (see **Table 1**). In all the other clusters, strong magnetic exchange interactions between individual paramagnetic ions results in high-spin ground states. Magnetometric and HFEPR results are in perfect agreement for **[CoMn]**, where the ground spin state is S = 4. They are also in reasonable agreement for **[CoCo]**, where the ground spin state is S = 2. The difference in the magnitude of the zfs parameter D in the latter is interpreted as stemming from the inability of magnetometry to accurately determine the zfs in the presence of strong rhombicity (large E/D). HFEPR results for **[CoNi]** were inconclusive. The unstable complex **[CoFe]** was not investigated by HFEPR.

Table 1. Magnetic properties of the square compounds

Comp.	M(II)	$S_{M(II)}$	$g_{M(II)}$	J (cm^{-1})	Ground state	D (cm^{-1}) (magnetometry)	D (cm^{-1}) (HFEPR)	E (cm^{-1}) (HFEPR)
[CoMn]	Mn	5/2	2.02	–10	S = 4	–0.24	–0.22	–0.009
[CoFe]	Fe	2	2.12	–9	S = 3	–2.98		
[CoCo]	Co	3/2	2.40	–8.0	S = 2	–2.74	–4.49	–1.31
[CoNi]	Ni	1	2.8	–6	S = 1	–6		
[CoZn]	Zn	0	0	~0	2 × (S = 1/2)	0	0	0

Conclusions

The performed magnetometric and HFEPR studies showed that the newly prepared molecular squares exhibit significant magnetic anisotropy, making them candidates for a construction of extended polynuclear assemblies characterized by potentially interesting properties such as Single Molecule Magnetism.

Acknowledgements

This research was supported by NSF (PI grant CHE-9906583), DOE (grant DE-FG03-02ER45999) and the NHMFL.