Electronic supplementary information (ESI)

New Copper(II)-Centered Complexes with Organometallic Donor-Acceptor Substituted Unsymmetrical Schiff Base Ligands^{†‡}

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Fig. S1 Experimental (top) and simulated (bottom) ion peaks of the cationic entity of the ionic complex **5**.

EPR Spectroscopy in fluid and frozen glass solution

The X-band EPR spectra of neutral binuclear (**3** and **6**) and of ionic trinuclear (**5** and **7**) unsymmetrical Schiff base derivatives have been recorded in $CH_2Cl_2/C_2H_4Cl_2$ (1/1) mixture at both 298 and 68 K. The EPR parameters extracted from the fluid and frozen glass solution spectra are collected in Table S1.

Table S1 EPR parameters for Cu^{II}-centered Schiff base compounds measured in fluid and frozen glass solutions^{*a*}

<i>T</i> (K)	298			68			
Compd.	$g_{ m iso}$	A _{cu} (G)	A _N (G)	<i>g</i> //	A _{//} (G)	$G \bot$	g(ΔMS = ±2)
3	2.102	90.5	13.3	2.20	200.0	2.047	4.18
5	2.099	90.0	13.3	2.20	200.3	2.059	-
6	2.101	90.0	13.3	2.20	213.0	2.064	-
7	2.100	86.0	13.3	2.216	192.0	2.051^{b}	4.200

^{*A*} Dichloromethabe/1,2-dichloroethane (1/1) mixture. ^{*b*} With a coupling constant $A_N = 15.5$ G.

At 298 K in solution (Fig. S2, top), the EPR spectra of the four complexes are very similar and point out partially resolved superhyperfine structure (3 lines, $a_N = 13.3$ G) superimposed on the quartet hyperfine structure, arising from the interaction of an unpaired electron with a single copper nucleus (I = 3/2), centred at g_{iso} ca. 2.100 with hyperfine coupling A_{iso} values of ca. 90 G (see Table S1).¹ Those data are consistent with a monomeric copper(II) species (S = 1/2), with the Cu²⁺ ion in a square planar coordination environment comprising two nitrogen nuclei.^{2,3} The glassy solution spectra (68 K) exhibit an asymmetric signal for the $\Delta MS = \pm 1$ transition (Fig. S2, bottom) with identical $g_{J} = 2.20$ and g_{\perp} values ranging between 2.047 and 2.064, with an average A_{J} coupling term of 200 G (Table S1). In addition, spectra of **3** and **7** showed very weak forbidden $\Delta MS = \pm 2$ half field transition (Fig. S2, insert), arising from very small dipolar through-space interactions between copper(II) ions in a dimeric species with triplet-state configuration (S = 1).^{4,5} The nature of the changes detected in the EPR spectra of **3** and **7** between room and low temperatures suggests that there is a monomer-dimer equilibrium in solution, for which the triplet species represents only a very minor fraction.



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Fig. S2 X-band EPR spectra of 3 recorded in $CH_2Cl_2/C_2H_4Cl_2$ (1/1) mixture at 298 K (top) and 68 K (bottom).



Fig. S3 Temperature dependences of $\chi_M T$ and ${\chi_M}^{-1}$ of powdered sample of complex **7**. Red lines correspond to the best agreement with Bleaney-Bowers equation and Curie-Weiss law (see main text) for $\chi_M T$ and ${\chi_M}^{-1}$, respectively.

References

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