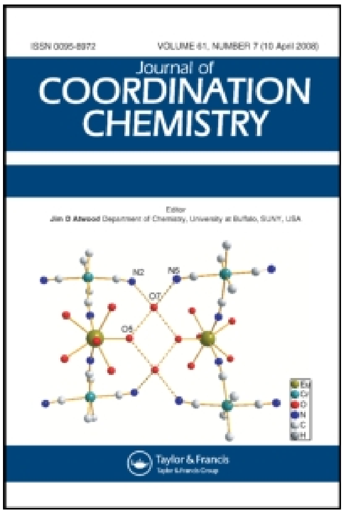

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SYNTHESIS AND CHARACTERISATION OF POLYOXOTUNGSTATE COMPOUNDS WITH COMPLEX COPPER AND COBALT CATIONS

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SYNTHESIS AND CHARACTERISATION OF POLYOXOTUNGSTATE COMPOUNDS WITH COMPLEX COPPER AND COBALT CATIONS

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Salts of the heteropolytungstates $[PW_{11}M(H_2O)O_{39}]^{5-}$, M = Cu, Co, Mn, with the following complex cations were prepared: $[Cu(LL)_2(H_2O)]^{2+}$, $[Cu(LL)_3]^{2+}$, LL = 1,10-phenantroline (phen), 2,2′-bipyridine (bipy), $[Cu(phen)_2Cl]^{+}$, $[Co(bipy)_2(CO_3)]^{+}$, and $[Co(phen)_3]^{2+}$. Compounds with $[SiW_{11}M(H_2O)O_{39}]^{6-}$, M = Cu, Co, Mn, and the cations $[Cu(LL)_2(H_2O)]^{2+}$, and $[Co(bipy)_2(CO_3)]^{+}$ were also prepared. Synthesis was carried out in aqueous or nitromethane solutions. The compounds were characterised by elemental and thermal analysis and spectroscopic techniques. Spectroscopic properties and the thermal stability of the polyanions in these compounds could thus be compared with those of simpler salts. BET surface areas were determined. Except for salts of $[Cu(bipy)_3]^{2+}$, the compounds decompose on heating at temperature above 200°C, the exact temperature depending on the cation. Some are stable up to 300°C. For salts of the $[Cu(LL)_2(H_2O)]^{2+}$ cations, more detailed thermal studies were performed, based on the infra red spectra of the decomposition products obtained at several temperatures.

Keywords: Polyoxometalate; Metal substituted polyoxotungstate; Tungstophosphate; Tungstosilicate; Copper complex; Cobalt complex

INTRODUCTION

Polyoxometalates constitute a large class of anions that find applications in a wide variety of fields [1–4]. The polyoxotungstates with the

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Keggin structure are among the most studied polyoxometalates. These include the parent Keggin anions, $[XW_{12}O_{40}]^{n-}$, the lacunary $[XW_{11}O_{39}]^{(n+4)-}$, and the metal substituted anions, $[XW_{11}M(L)O_{39}]^{p-}$, $X=P$, Si, B, and others, $M=$ transition or p-block metal ion, $L=H_2O$ or other monodentate ligand [1]. The association of Keggin type polyoxotungstates with cations different from the "traditional" ones (group 1 metals, NH_4^+, low tetra-alkylammonium cations) has recently been shown to provide very interesting compounds with relevant new properties. These include new magnetic [5, 6], conducting [6] and support [7] properties, among others.

The application of polyoxotungstates in homogeneous and heterogeneous catalysis of a large number of reactions is well known [8 – 13]. A particularly interesting line of study concerns the synthesis of bi-functional catalysts through the association of Keggin polyoxoanions with transition metal complex cations, first described by Siedle *et al.* [14]. These researchers have prepared and studied stable compounds with highly reactive coordinatively unsaturated cationic species stabilised in the lattice formed by the metal oxide anionic clusters [15, 16].

Copper and its complexes are important reagents or catalysts in the reactions of organic compounds. The importance of copper (II) species as catalysts in several types of oxidative reactions has been reviewed [17, 18]. In view of preparing possible bi-functional catalysts, we decided to study compounds of the transition metal substituted polyoxoanions $[XW_{11}M(H_2O)O_{39}]^{(n+2)-}$, $X=P$, Si, $M=Cu^{2+}$, Co^{2+}, Mn^{2+}, with copper(II) complexes of formula $[Cu(LL)_2(L')]^{2+}$, and $[Cu(LL)_3]^{2+}$, $LL=2,2'$-bipyridine (bipy), o-phenantroline (phen) and $L'=$ monodentate ligand. The synthesis and characterisation of the prepared compounds is described in this work. For comparison, compounds with some cobalt complexes were also studied.

EXPERIMENTAL

Synthesis

All chemicals were used as received from suppliers. The following compounds were prepared by reported procedures: $K_5[PW_{11}M(H_2O)O_{39}]\cdot nH_2O$ and $K_6[SiW_{11}M(H_2O)O_{39}]\cdot nH_2O$, $M=$ Cu, Co, Mn [19], $(TBA)_4H[PW_{11}M(H_2O)O_{39}]\cdot nH_2O$, TBA = tetrabutylammonium, $M=$ Cu, Co, Mn [20], $[Cu(phen)_2(H_2O)](NO_3)_2$ [21], $[Cu(bipy)_2(ONO_2)](NO_3)\cdot H_2O$ [22],

$[Cu(LL)_2Cl]Cl \cdot 3H_2O$, LL = phen, bipy [23], $[Cu(LL)_3](NO_3)_2 \cdot nH_2O$, LL = phen, bipy [24], $[Cu(bipy)_2(NCS)](SCN)$ [25], $[Co(bipy)_2(CO_3)](NO_3) \cdot H_2O$ [26], $[Co(phen)_3][Sb_2(C_4H_2O_6)_2] \cdot 7H_2O$ [27].

$[Cu(phen)_2(H_2O)]_{2.5}[PW_{11}M(H_2O)O_{39}] \cdot nH_2O$ and $Cu(phen)_2(H_2O)]_3[SiW_{11}M(H_2O)O_{39}] \cdot nH_2O$, M = Cu, Co, Mn

Aqueous solutions of the heteropolyanion (K^+ salts, 0.09 mmol, 5 cm^3) and $[Cu(phen)_2(H_2O)](NO_3)_2$ (slight excess over stoichiometric proportion, 20 cm^3) were prepared. The two solutions were heated and the copper complex slowly added to the polyoxotungstate, with stirring. The obtained precipitates were filtered (still warm), washed with hot water and dried in a vacuum desiccator.

$[Cu(phen)_3]_{2.5}[PW_{11}M(H_2O)O_{39}] \cdot nH_2O$ and $[Cu(bipy)_3]_{2.5}[PW_{11}M(H_2O)O_{39}] \cdot nH_2O$, M = Cu, Co, Mn

The procedure described above was applied with solutions at room temperature and starting with $[Cu(phen)_3](NO_3)_2 \cdot 2H_2O$ or $[Cu(bipy)_3](NO_3)_2$.

$[Cu(bipy)_2(H_2O)]_{2.5}[PW_{11}M(H_2O)O_{39}] \cdot nH_2O$ and $[Cu(bipy)_2(H_2O)]_3[SiW_{11}M(H_2O)O_{39}] \cdot nH_2O$, M = Cu, Co, Mn

A process similar to that described above was used, starting with $[Cu(bipy)_2(ONO_2)](NO_3) \cdot H_2O$.

$[Cu(phen)_2Cl]_5[PW_{11}M(H_2O)O_{39}] \cdot nH_2O$, M = Cu, Co, Mn

Solutions in nitromethane of $(TBA)_4H[PW_{11}M(H_2O)O_{39}] \cdot nH_2O$ (0.05 mmol, 10 cm^3) and $[Cu(phen)_2Cl]Cl \cdot 3H_2O$ (slight excess over stoichiometry, 15 cm^3) were prepared. The copper complex was slowly added to the polyoxotungstate, with stirring, at room temperature. The obtained precipitates were filtered, washed with several portions of nitromethane and dried in a vacuum desiccator.

$[Co(bipy)_2(CO_3)]_5[PW_{11}M(H_2O)O_{39}] \cdot nH_2O$ and $[Co(bipy)_2(CO_3)]_6[SiW_{11}M(H_2O)O_{39}] \cdot nH_2O$, $M = Cu, Co, Mn$

Aqueous solutions of the heteropolyanion (K^+ salts, 0.05 mmol, 10 cm^3) and $[Co(bipy)_2(CO_3)](NO_3) \cdot H_2O$ (slight excess over stoichiometry, 20 cm^3) were prepared. The product was obtained as described above for $[Cu(phen)_3]^{2+}$ salts.

$[Co(phen)_3]_{2.5}[PW_{11}M(H_2O)O_{39}] \cdot nH_2O$, $M = Cu, Co, Mn$

A process similar to the described above for $[Cu(phen)_2Cl]^+$ salts was used, starting with the compound $[Co(phen)_3][(Sb_2(C_4H_2O_6)_2] \cdot 7H_2O$.

Analysis

Elemental analyses (P, W, Cu, Co and Mn) were performed by ICP spectrometry (University of Aveiro, Central Analysis Laboratory). Solutions were prepared by dissolving the compounds in an alkaline solution of edta at $pH = 10$ or 12 (prepared in turn by dissolving Na_2edta in water, 3.0 g/L, and adjusting the pH with NaOH) for the compounds with copper or cobalt complex cations, respectively. Hydration water was determined from weight loss to 140°C. Values of total weight loss were calculated from thermogravimetric analyses performed to 700°C, assuming decomposition to a mixture of oxides. Analytical results (see supplementary material available from the authors on request) were in agreement with the proposed formulae.

Physical Measurements

Thermogravimetric analyses (TG) between 30–700°C were carried out in air, at 5 and 10°C min^{-1} rate, on a Mettler M3 thermobalance equipped with a TC 10A microprocessor. Diffuse reflectance spectra (400–1200 nm) were recorded on a Shimadzu 3100 spectrophotometer, using MgO as reference. Infrared absorption spectra (400–4000 cm^{-1}) were recorded on a Mattson 7000 FTIR spectrometer, using KBr pellets. Powder EPR spectra were recorded with a Bruker ESP 300E spectrometer at 298 and 77 K. The spectra were calibrated against diphenylpicrylhydrazyl (dpph; $g = 2.0037$), and the magnetic field was calibrated by the use of Mn(II) in MgO. Typical experimental conditions used were as follows: microwave frequency

9.53 GHz, modulation frequency 100 kHz, modulation amplitude 0.1–0.5 mT and microwave power 5 mW. BET surface areas were measured on Micromeritics Gemini equipment. Samples were evacuated at 150°C for 8 h as a pre-treatment.

RESULTS AND DISCUSSION

Synthesis

The preparation of compounds of the tungstophosphate anions $[PW_{11}M(H_2O)O_{39}]^{5-}$, $M = Cu$, Co, Mn, with the cations $[Cu(phen)_2(H_2O)]^{2+}$, $[Cu(phen)_3]^{2+}$, and $[Cu(bipy)_3]^{2+}$ is straightforward, as precipitation occurs when aqueous solutions of the ions are mixed. Salts of $[Cu(bipy)_2(H_2O)]^{2+}$ were also prepared, using a salt of $[Cu(bipy)_2(ONO_2)]^{+}$ as starting material. Similar compounds with $[SiW_{11}M(H_2O)O_{39}]^{5-}$ may also be obtained, but only a few were studied.

Aqueous solutions cannot be used to prepare compounds of potentially hydrolysable cations, such as $[Cu(LL)_2(Cl)]^{+}$ or $[Cu(bipy)_2(NCS)]^{+}$. Preparation of tungstophosphate compounds with $[Cu(phen)_2(Cl)]^{+}$ (but not with $[Cu(bipy)_2(Cl)]^{+}$ or $[Cu(bipy)_2(NCS)]^{+}$) was performed in nitromethane, starting with tetrabutylammonium salts of the polyanions. Compounds with the cobalt complexes $[Co(bipy)_2(CO_3)]^{+}$ and $[Co(phen)_3]^{2+}$ were precipitated from water and nitromethane, respectively. The prepared compounds (Tab. I) are generally amorphous powders, insoluble in water and common organic solvents.

Characterisation

Several spectroscopic techniques were used to study the complexes. The results point to the fact that the compounds are salts of the heteropolyanions and the cations used in their preparation (except for the $[Cu(bipy)_2(H_2O)]^{2+}$ compounds prepared by hydrolysis of $[Cu(bipy)_2(ONO_2)]^{+}$). Elemental and thermal analyses were used to determine the formula presented in Table I.

Infrared Spectroscopy

The infrared spectra present bands corresponding to the superposition of anion and cation spectra. The positions of the bands corresponding to each

TABLE I Heteropolytungstates salts of copper and cobalt complexes

1	$[Cu(phen)_2(H_2O)]_{5/2}[PW_{11}Cu(H_2O)O_{39}] \cdot 5H_2O$	**16**	$[Cu(phen)_3]_{5/2}[PW_{11}Cu(H_2O)O_{39}] \cdot 8H_2O$
2	$[Cu(phen)_2(H_2O)]_{5/2}[PW_{11}Co(H_2O)O_{39}] \cdot 7H_2O$	**17**	$[Cu(phen)_3]_{5/2}[PW_{11}Co(H_2O)O_{39}] \cdot 8H_2O$
3	$[Cu(phen)_2(H_2O)]_{5/2}[PW_{11}Mn(H_2O)O_{39}] \cdot 6H_2O$	**18**	$[Cu(phen)_3]_{5/2}[PW_{11}Mn(H_2O)O_{39}] \cdot 11H_2O$
4	$[Cu(phen)_2(H_2O)]_3[SiW_{11}Cu(H_2O)O_{39}] \cdot 7H_2O$	**19**	$[Cu(bipy)_3]_{5/2}[PW_{11}Cu(H_2O)O_{39}] \cdot 6H_2O$
5	$[Cu(phen)_2(H_2O)]_3[SiW_{11}Co(H_2O)O_{39}] \cdot 6H_2O$	**20**	$[Cu(bipy)_3]_{5/2}[PW_{11}Co(H_2O)O_{39}] \cdot 7H_2O$
6	$[Cu(phen)_2(H_2O)]_3[SiW_{11}Mn(H_2O)O_{39}] \cdot 6H_2O$	**21**	$[Cu(bipy)_3]_{5/2}[PW_{11}Mn(H_2O)O_{39}] \cdot 6H_2O$
7	$[Cu(bipy)_2(H_2O)]_{5/2}[PW_{11}Cu(H_2O)O_{39}] \cdot 8H_2O$	**22**	$[Co(bipy)_2(CO_3)]_5[PW_{11}Cu(H_2O)O_{39}] \cdot 15H_2O$
8	$[Cu(bipy)_2(H_2O)]_{5/2}[PW_{11}Co(H_2O)O_{39}] \cdot 9H_2O$	**23**	$[Co(bipy)_2(CO_3)]_5[PW_{11}Co(H_2O)O_{39}] \cdot 15H_2O$
9	$[Cu(bipy)_2(H_2O)]_{5/2}[PW_{11}Mn(H_2O)O_{39}] \cdot 8H_2O$	**24**	$[Co(bipy)_2(CO_3)]_5[PW_{11}Mn(H_2O)O_{39}] \cdot 16H_2O$
10	$[Cu(bipy)_2(H_2O)]_3[SiW_{11}Cu(H_2O)O_{39}] \cdot 11H_2O$	**25**	$[Co(bipy)_2(CO_3)]_6[SiW_{11}Cu(H_2O)O_{39}] \cdot 19H_2O$
11	$[Cu(bipy)_2(H_2O)]_3[SiW_{11}Co(H_2O)O_{39}] \cdot 11H_2O$	**26**	$[Co(bipy)_2(CO_3)]_6[SiW_{11}Co(H_2O)O_{39}] \cdot 21H_2O$
12	$[Cu(bipy)_2(H_2O)]_3[SiW_{11}Mn(H_2O)O_{39}] \cdot 8H_2O$	**27**	$[Co(bipy)_2(CO_3)]_6[SiW_{11}Mn(H_2O)O_{39}] \cdot 28H_2O$
13	$[Cu(phen)_2Cl]_5[PW_{11}Cu(H_2O)O_{39}] \cdot 8H_2O$	**28**	$[Co(phen)_3]_{5/2}[PW_{11}Cu(H_2O)O_{39}] \cdot 8H_2O$
14	$[Cu(phen)_2Cl]_5[PW_{11}Co(H_2O)O_{39}] \cdot 8H_2O$	**29**	$[Co(phen)_3]_{5/2}[PW_{11}Co(H_2O)O_{39}] \cdot 9H_2O$
15	$[Cu(phen)_2Cl]_5[PW_{11}Mn(H_2O)O_{39}] \cdot 7H_2O$	**30**	$[Co(phen)_3]_{5/2}[PW_{11}Mn(H_2O)O_{39}] \cdot 10H_2O$

cation do not change significantly for the different compounds with heteropolyanions, and are similar to those of the simple nitrates and halides used as starting materials.

Keggin-type polyoxotungstates give characteristic infrared bands in the 1000–700 cm^{-1} region, assigned to W=O and W—O—W stretching vibrations [28, 29]. The frequencies of some of these bands in the spectra of the prepared compounds and in those of the corresponding potassium salts are presented in Table II. The shift of the W=O stretching vibration to lower frequencies is observed in the spectra of all prepared compounds when compared with those of the potassium salts. The lowering of the value of these frequencies with increasing size of the counter-cations has been attributed to smaller anion–anion interaction [29].

The ν_{as}(P—O) mode, observed in the 1110–1040 cm^{-1} region, is the most informative band in the spectra of the tungstophosphates. The vibration of the P—O bonds of the central PO_4 tetrahedron gives one band, at 1080 ± 1 cm^{-1}, in the spectra of the parent Keggin anion, $[PW_{12}O_{40}]^{3-}$, that does not change significantly with the counter-cation used [29, 30]. This band is split in two in the spectra of the lacunary $[PW_{11}O_{39}]^{7-}$ and of many $[PW_{11}M(H_2O)O_{39}]^{(7-m)-}$ anions (m = oxidation state of M). Generally, the value of splitting, $\Delta\nu$, is smaller for the metal substituted anions than for the lacunary anion, reflecting the higher symmetry of the former [28]. For these anions, the position of the two bands and the value of the corresponding $\Delta\nu$ vary with the counter-cation used. Spectra of TBA salts show, generally, smaller $\Delta\nu$ than K^+ salts [20, 28].

Table III gives $\Delta\nu$ for the polyoxotungstates in the studied compounds. Considering salts of the same counter-ion, $\Delta\nu$ was found to vary in the order $Cu^{2+} > Mn^{2+} > Co^{2+}$. The same order is known to occur for the K^+ [28] and TBA [20] salts. For the Co^{II} and Mn^{II} heteropolyanions,

TABLE II Characteristic W—O infrared absorption frequencies for heteropolytungstates with complex cations and potassium[a]

	Complex cations		*K^+*	
Anion	*$\nu(W{=}O_d)$*[b]	*$\nu(W{-}O_b{-}W)$*[b]	*$\nu(W{=}O_d)$*	*$\nu(W{-}O_b{-}W)$*
$[PW_{11}Cu(H_2O)O_{39}]^{5-}$	951 ± 3	882 ± 4	964	887
$[PW_{11}Co(H_2O)O_{39}]^{5-}$	950 ± 3	882 ± 3	961	886
$[PW_{11}Mn(H_2O)O_{39}]^{5-}$	948 ± 3	883 ± 3	959	886
$[SiW_{11}Cu(H_2O)O_{39}]^{6-}$	946 ± 2	899 ± 1	958	903
$[SiW_{11}Co(H_2O)O_{39}]^{6-}$	945 ± 2	899 ± 1	959	903
$[SiW_{11}Mn(H_2O)O_{39}]^{6-}$	948 ± 3	899 ± 5	959	903

[a] In cm^{-1}.
[b] Average values.

TABLE III P—O stretching vibration frequencies for the complex salts of heteropolyanions

	$[PW_{11}Cu(H_2O)O_{39}]^{5-}$			$[PW_{11}Co(H_2O)O_{39}]^{5-}$			$[PW_{11}Mn(H_2O)O_{39}]^{5-}$		
	ν_1, ν_2	aver[a]	$\Delta\nu$[b]	ν_1, ν_2	aver[a]	$\Delta\nu$[b]	ν_1, ν_2	aver[a]	$\Delta\nu$[b]
$[Cu(phen)_2(H_2O)]^{2+}$	1057 1103	1080	46	1057 1072(sh)	1065	15	1051 1076	1064	25
$[Cu(bipy)_2(H_2O)]^{2+}$	1060 1101	1081	41	1058 1072(sh)	1065	14	1052 1074	1063	22
$[Cu(phen)_2Cl]^{+}$	1057 1104	1081	47	1056 1072(sh)	1064	16	1051 1078	1065	27
$[Cu(phen)_3]^{2+}$	1044 1076 1105	1075	61	1051 1074	1063	23	1048 1089	1069	41
$[Cu(bipy)_3]^{2+}$	1045 1103	1074	58	1055 1073	1064	18	1046 1091	1069	45
$[Co(bipy)_2(CO_3)]^{+}$	1058 1102	1080	44	1055 1074	1065	19	1048 1076	1062	28
$[Co(phen)_3]^{2+}$	1058 1103	1081	45	1057 1072(sh)	1065	15	1051 1077	1064	26
K^{+}	1061 1101	1081	40	1058 1076	1067	18	1053 1080	1067	27
TBA^{+}	1067 1101	1084	34	1063		0	1057 1073(sh)	1065	16

[a] Average $= 1/2(\nu_1 + \nu_2)$.
[b] $\Delta\nu = \nu_2 - \nu_1$.

the observed $\Delta\nu$ values, with a few exceptions, are close to those of the corresponding K^+ salts. The values found for $[PW_{11}Cu(H_2O)O_{39}]^{5-}$ are generally higher, indicating that the distortion of the environment around copper in this anion is more pronounced than for the other metals. Of all the complex cations studied, $[Cu(LL)_3]^{2+}$, LL = phen, bipy, seem to have the largest effect in the distortion of the anion, as, for a given anion, the values of $\Delta\nu$ are higher for these counter-cations than for all the others studied.

It is accepted that comparison of the values of $\Delta\nu$ observed for a series of related metal substituted Keggin anions provides an indirect measure of the strength of the interaction of the metal M with the oxygen of the central PO_4 group [28, 31]. A very large $\Delta\nu$ may indicate that the metal is not bound to the central oxygen [31, 32]. The results presented here, however, indicate that comparison of $\Delta\nu$ values for compounds with different counter-cations may be misleading and should not be attempted. EPR results (see below) obtained for the compounds with $[PW_{11}Cu(H_2O)O_{39}]^{5-}$ and cobalt complex cations indicate that Cu(II) in the polyanion is hexacoordinated, in spite of the fact that the splitting observed for these compounds (as well as for some salts of $[PW_{11}Mn(H_2O)O_{39}]^{5-}$) is close to that of $K_7[PW_{11}O_{39}] \cdot nH_2O$ ($\Delta\nu = 45\,cm^{-1}$) [28].

When the split of the P—O stretching band is observed, the average value of the two observed frequencies seem to be reasonably constant for a given anion (Tab. III). These average values have been related to the strength of the P—O bonding in the central PO_4 [33]. This value is higher for the copper anions than for the cobalt or manganese analogues, as found, also, for other salts [20, 28].

Electronic Spectroscopy

Diffuse reflectance spectra may show the anion and cation bands; however the latter were stronger, reflecting the stoichiometric composition of the salts and thus, in most cases, obscuring completely the anion bands in the visible region. Compounds with $[Cu(LL)_2(X)]^{n+}$, $X = Cl^-$, H_2O, show a broad peak in the 745–780 nm range, with a shoulder around 950 nm (Fig. 1a). Trigonal bipyramidal $[Cu(LL)_2(X)]^{n+}$ usually give spectra with one visible band [21, 23]. The splitting of this band was found to indicate distortion towards a square pyramidal structure around copper [23]. The spectra of the $[Cu(LL)_3]^{2+}$ compounds have also a maximum near 730 nm with a ill-defined shoulder at higher wavelength, but they were easily distinguished from those of penta-coordinated copper. It is probable that, in these counter-cations, copper has the distorted octahedral environment found for

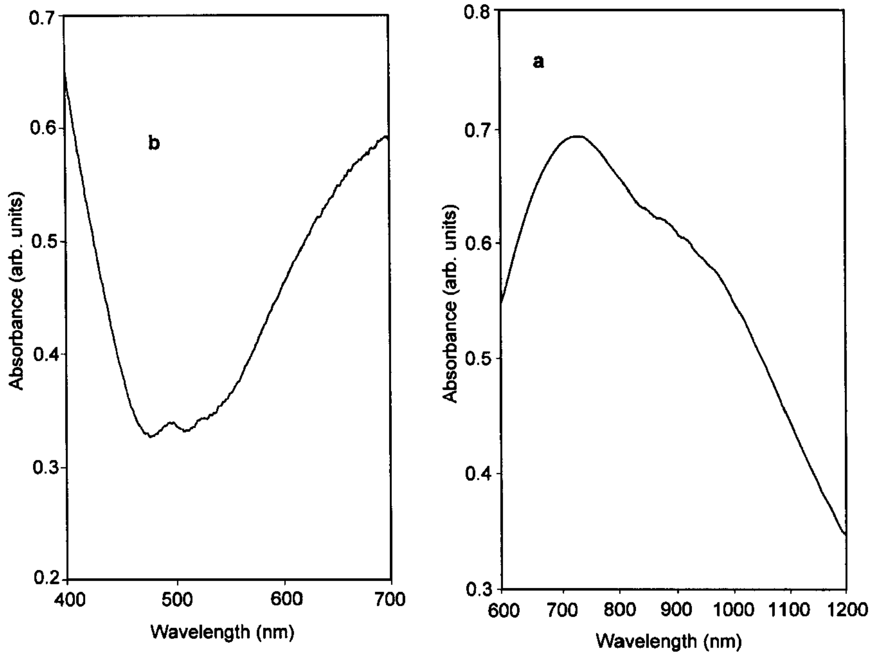

FIGURE 1 Diffuse reflectance spectra in the near infrared (a) and visible (b) region of $[Cu(bipy)_2(H_2O)]_{5/2}[PW_{11}Co(H_2O)O_{39}] \cdot 9H_2O$.

perchlorate salts [24]. For the compounds of $[PW_{11}Co(H_2O)O_{39}]^{5-}$ with $[Cu(LL)_2(H_2O)]^{2+}$, the spectra show two small peaks around 495 and 525 nm, respectively, assigned to transitions of the Co(II)-containing chromophore (Fig. 1b). Weakley was the first to report that the diffuse reflectance spectra of the $[PW_{11}Co(H_2O)O_{39}]^{5-}$ anions are cation dependent and, in some cases (that were called abnormal reflectance spectra), markedly different from solution spectra [34]. Salts of very large cations presented that abnormal reflectance spectra [34]. The position and relative intensities of the peaks referred above are in complete agreement with this observation. For the $[SiW_{11}Co(H_2O)O_{39}]^{6-}$ compounds, on the other hand, no abnormal reflectance spectra have been reported [34]. Our compounds with $[Cu(LL)_2(H_2O)]^{2+}$ showed only one ill-defined peak, at ca. 550 nm.

EPR Spectroscopy

EPR spectra of all the prepared compounds were measured. Under the experimental conditions used, compounds **23**, **26** and **29** (Tab. I) are EPR silent. For the other compounds two type of EPR spectra were observed, spectra that show an intense *pseudo*-isotropic signal, compounds **1**–**21**, and spectra that are typical of magnetically dilute paramagnetic metal centres, compounds **22**, **24**, **25**, **27**, **28**, **30**.

The compounds that exhibit *pseudo*-isotropic EPR spectra are those for which the counter-cations are copper complexes. The EPR spectra exhibit g values in the range 2.11–2.12, values that are similar to those of spectra of the copper complexes in the absence of polytungstate anion. No g features due to the polyanion could be observed. (Figs. 2a–c). The EPR signals are due to the copper centres of cations which exist in large molar excess to other paramagnetic species in the solid, and thus prevent detection of signals of paramagnetic centres in the polyanions, due to broadening of the copper signals caused by spin–spin interactions. No information on the coordination mode of the polyanion could be obtained.

Compounds of $[XW_{11}M(H_2O)O_{39}]^{n-}$, $X = P$ and Si, $M = Cu(II)$, and Mn(II), with the cations $[Co(bipy)_2(CO_3)]^+$ and $[Co(phen)_3]^{2+}$, exhibit magnetically dilute EPR spectra. Compounds **22**, **25**, **28**, for which $M = Cu(II)$, show spectra of axial type, with two non-overlapping, well-resolved g regions and with copper hyperfine couplings ($^{63}Cu/^{65}Cu$, $I = 3/2$) in the region of low magnetic field (Fig. 2d). The $g_{\parallel}$ (2.42–2.43) and $|A_{\parallel}|$ values (81–85 gauss) are similar to those of the related potassium salts, $K_n[XW_{11}Cu(H_2O)O_{39}] \cdot nH_2O$, $X = P$ ($n = 5$) and Si ($n = 6$) [35, 36], and to those of Cu(II) in oxidic solids [37]. As $[Co(bipy)_2(CO_3)]^+$ is diamagnetic and $[Co(phen)_3]^{2+}$ does not exhibit X-band EPR signals, the EPR signal is due to Cu(II) centres in the polyanions, which are magnetically diluted in the oxygen matrix.

The similarity of the EPR spectra with those of the homologous potassium compounds $K_5[PW_{11}Cu(H_2O)O_{39}] \cdot nH_2O$ and $K_6[SiW_{11}Cu(H_2O)O_{39}] \cdot nH_2O$ [35, 36] can be extended to support the same orientation scheme for the tensor axes in these compounds: $g_{\parallel} = g_1$, $g_{\perp} = 1/2(g_2 + g_3)$, where g_1 and g_3 refer to the lowest and highest magnetic field g values, respectively (obviously, $A_{\parallel} = A_1$; $A_{\perp} = 1/2(A_2 + A_3)$). In this context, the observations that $g_{\parallel} > g_{\perp}$, $g_{\parallel} = 2.42–2.43$ and $|A_{\parallel}| = 81–85$ Gauss imply a B_{1g} ($3d_{x^2-y^2}$) ground state for these compounds [38], and an O_h-tetragonally elongated geometry for Cu(II) in the matrix, as observed for the compounds referred to above. Thus, both the $[PW_{11}O_{39}]^{7-}$ and $[SiW_{11}O_{39}]^{8-}$ anions act as a pentadentate ligand, possibly with long Cu—O bonds, and with the sixth co-ordination position being occupied by a water molecule [35, 36].

The compounds with the polyanions $[PW_{11}Mn(H_2O)O_{39}]^{5-}$ and $[SiW_{11}Mn(H_2O)O_{39}]^{6-}$, **24**, **27** and **30**, show EPR features due to the

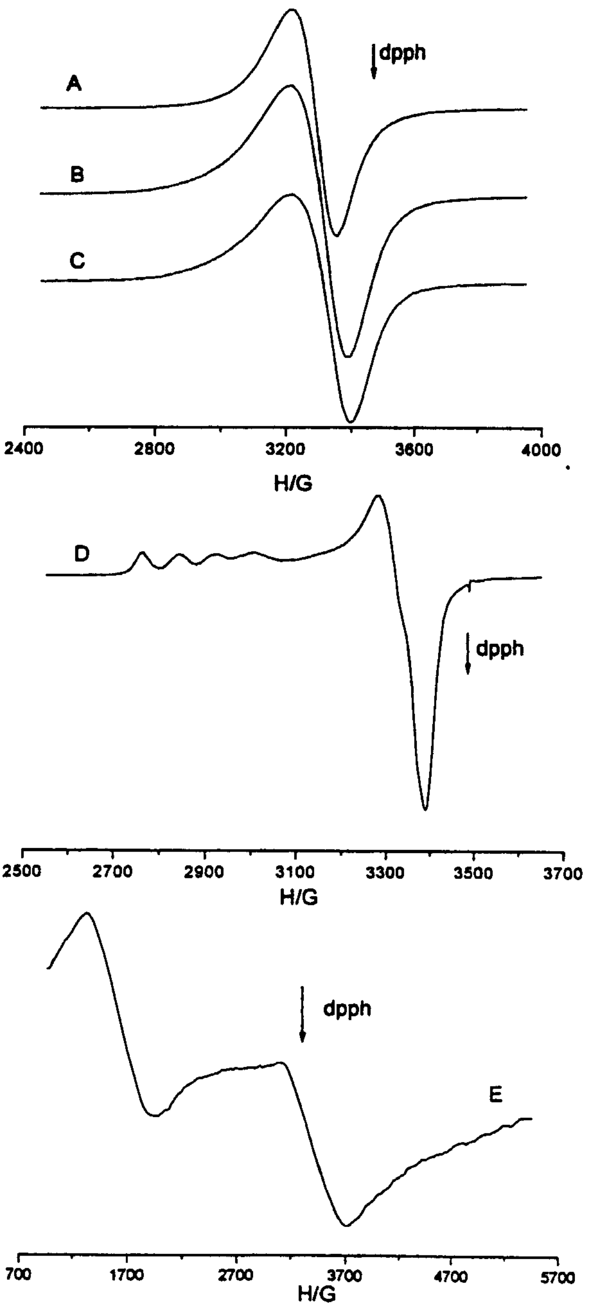

FIGURE 2 Powder EPR spectra (room temperature) of (a) $[Cu(phen)_3](NO_3)_2 \cdot 2H_2O$; (b) $[Cu(phen)_3]_{5/2}[PW_{11}Cu(H_2O)O_{39}] \cdot 8H_2O$; (c) $[Cu(phen)_3]_{5/2}[PW_{11}Co(H_2O)O_{39}] \cdot 8H_2O$; (d) $[Co(bipy)_2(CO_3)]_5[PW_{11}Cu(H_2O)O_{39}] \cdot 15H_2O$; (e) $[Co(phen)_3]_{5/2}[PW_{11}Mn(H_2O)O_{39}] \cdot 10H_2O$.

Mn(II) ion: two very broad and equally intense signals at $g \approx 1.99$ and $g \approx 4.3-4.4$ (Fig. 2e); no hyperfine splitting due to coupling to ^{55}Mn, $I = 5/2$ could be detected in any of the two g regions. It is known that complexes of Mn(II) in a nearly octahedral symmetry, for which the zero field splitting parameters, D and E, are approximately zero, exhibit only the $\Delta m_s = +1/2 \leftrightarrow -1/2$ transition at $g \approx 2.00$ with hyperfine coupling to Mn, resulting in a sextet with $A_{\mathrm{Mn}} \approx 90$ gauss; the others four non-Kramers transitions are broadened and hidden under this central band [39, 40]. Contrastingly, complexes with tetragonal or trigonal distortions have values of D or/and E different from zero, so that other lines, both up-field and down-field, due to the transitions from the $m_s = 5/2, 3/2, -3/2$ and $-5/2$ states can be observed [39–41]. The observation of EPR features outside the $g \approx 2.00$ region for compounds **24**, **27** and **30**, suggests that the Mn(II) in the polyanion has a distorted six coordinate geometry, probably similar to that observed for the homologous Cu based polyanions.

Thermal Decomposition Studies

Thermogravimetric analyses were performed for all the compounds. These are all heavily hydrated. Weight loss at temperatures below 140°C was attributed to the loss of water of crystallisation. The decomposition of the dehydrated salts took place in several steps, generally at temperatures above 200°C, except for the $[\mathrm{Cu(bipy)_3}]^{2+}$ salts, that started to decompose at about 150°C. On the other hand, salts of $[\mathrm{Cu(phen)_2(H_2O)}]^{2+}$ with the $[\mathrm{PW_{11}}M\mathrm{(H_2O)O_{39}}]^{5-}$ are stable up to 300°C.

For salts of the same cation and different anions, the form of the thermogram and the decomposition temperatures did not vary much. Compounds with phen started to decompose and finished the decomposition at slightly higher temperatures than the bipy analogues. Exceptions were found for $[\mathrm{Cu(bipy)_2(H_2O)}]_{2.5}[\mathrm{PW_{11}Cu(H_2O)O_{39}}] \cdot 8\mathrm{H_2O}$ and $[\mathrm{Cu(bipy)_3}]_{2.5}[\mathrm{PW_{11}Cu(H_2O)O_{39}}] \cdot 6\mathrm{H_2O}$, for which the weight loss ended at a temperature considerably higher (about 150°C) than for the other salts with the same counter-cations and higher than the analogues with phen.

Infra red spectra of the decomposition residues, after thermogravimetric analysis ended at several temperatures between 250°C and 500°C, were obtained for the compounds with the $[\mathrm{Cu}(LL)_2\mathrm{(H_2O)}]^{2+}$ cations. After heating any of the tungstophosphate compounds up to 350–400°C, the infrared spectra of the product show one band at 1080 cm^{-1}, characteristic of the parent Keggin anion $[\mathrm{PW_{12}O_{40}}]^{3-}$ [29, 30], as observed in the example of Figure 3. Other bands may be observed, however, simultaneously with those of the $[PW_{12}O_{40}]^{3-}$ anion, depending on the compound studied. The formation of $[PW_{12}O_{40}]^{3-}$ as an intermediate in the thermal decomposition

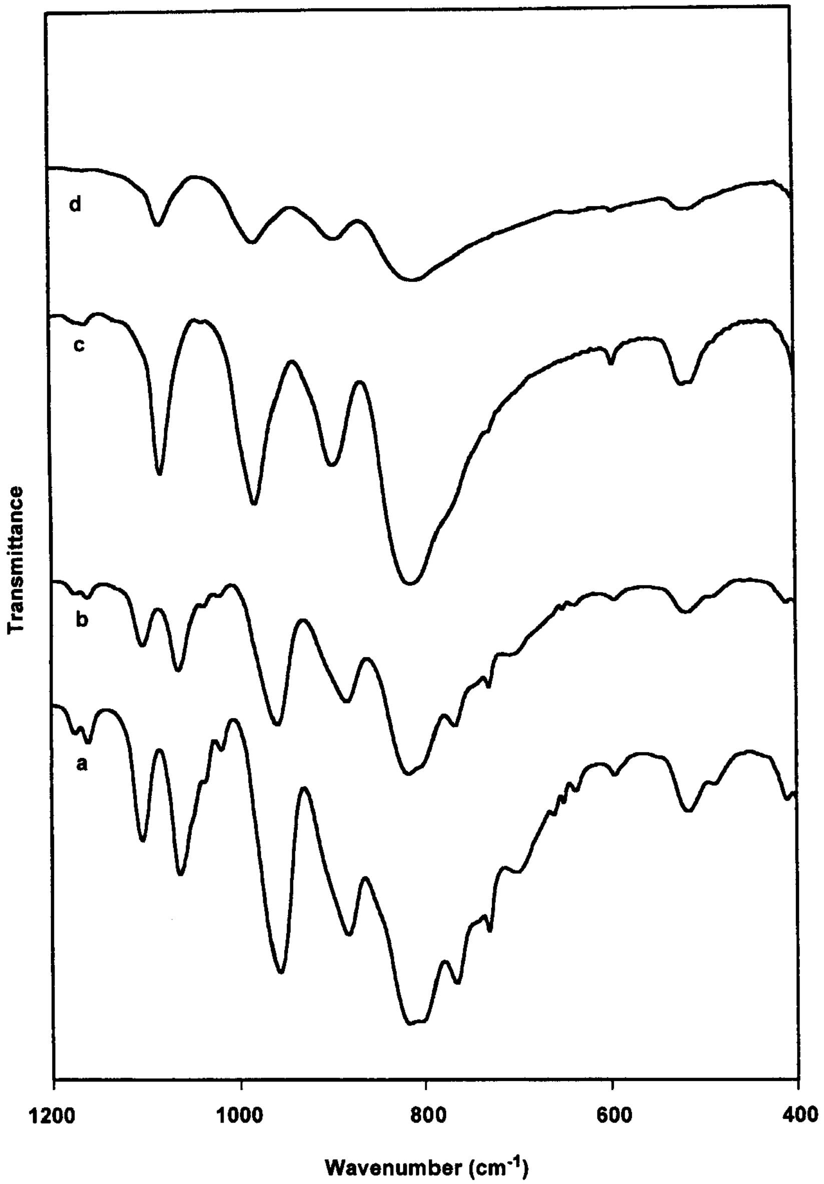

FIGURE 3 Infrared spectra of (a) $[Cu(bipy)_2(H_2O)]_{5/2}[PW_{11}Cu(H_2O)O_{39}]\cdot 8H_2O$ and after thermal decomposition up to (b) 300°C , (c) 350°C and (d) 400°C.

of the transition metal substituted Keggin polyoxotungstates had been found to occur for the tetrabutylammonium salts, but not for the corresponding potassium compounds [20].

The identification of $[SiW_{12}O_{40}]^{4-}$ based on the infrared spectra of the decomposition products obtained after thermogravimetry up to 400°C is less straightforward. Several bands observed for the salts with complex cations shift to the position of those observed for compounds like $H_4[SiW_{12}O_{40}]$ [29] or $Cu_2[SiW_{12}O_{40}]$. This may be considered an indication that the parent Keggin anion is formed during the decomposition of the studied silicon compounds, but no conclusive proof was found. Finally, at 700°C all the compounds had decomposed to what is considered a mixture of oxides.

Surface Area Determinations

BET surface areas were determined for several compounds. Compounds with copper complex cations present larger BET surface area than analogous potassium or tetrabutylammonium salts, whereas compounds with cobalt counter-cations have negligible BET values. The values found for the compounds with copper counter-cations are mostly in the range $10-20\,m^2\,g^{-1}$ (Tab. IV). These values are low in comparison with those of some salts of the parent Keggin anions. It is known that hydrated salts of $[XW_{12}O_{40}]^{n-}$ with cations like Na^+ or Mg^{2+} have low surface areas ($1-15\,m^2\,g^{-1}$) whereas salts of cations like Cs^+ have surface area values in the $50-200\,m^2\,g^{-1}$ range [11]. Variation of the precipitation conditions could, possibly, lead to compounds with larger values of surface area, but this work was not attempted.

TABLE IV Selected values of BET surface area

Compound	*Specific surface area*[a]
$K_5[PW_{11}M(H_2O)O_{39}]$[b]	< 0.5
$K_6[SiW_{11}M(H_2O)O_{39}]$[b]	< 0.5
$(TBA)_4H[PW_{11}M(H_2O)O_{39}]$[b]	< 0.5
$[Cu(phen)_2(H_2O)]_{2.5}[PW_{11}Cu(H_2O)O_{39}]$	11.3
$[Cu(phen)_2(H_2O)]_{2.5}[PW_{11}Co(H_2O)O_{39}]$	12.7
$[Cu(phen)_2(H_2O)]_3[SiW_{11}Cu(H_2O)O_{39}]$	18.9
$[Cu(phen)_2(H_2O)]_3[SiW_{11}Co(H_2O)O_{39}]$	20.3
$[Cu(phen)_2Cl]_5[PW_{11}Mn(H_2O)O_{39}]$	12.9
$[Cu(phen)_3]_{2.5}[PW_{11}Cu(H_2O)O_{39}]$	16.8
$[Cu(phen)_3]_{2.5}[PW_{11}Mn(H_2O)O_{39}]$	8.2

[a] $m^2\,g^{-1}$.
[b] M = Cu, Co, Mn.

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References

[1] M. T. Pope, *Heteropoly and Isopolyoxometalates* (Springer, Berlin, 1983).

[2] M. T. Pope and A. Muller (Eds.), *Polyoxometalates: from platonic solids to antirectroviral activity* (Kluwer, Dordrecht, 1994).

[3] J. T. Rhule, C. L. Hill, D. A. Judd and R. F. Schinazi, *Chem. Rev.* **98**, 327 (1998).

[4] D. E. Katsoulis, *Chem. Rev.* **98**, 359 (1998).

[5] E. Coronado and C. J. Gomez-Garcia, *Chem. Rev.* **98**, 273 (1998), and references therein.

[6] L. Ouahab, *Chem. Mater.* **9**, 1909 (1997), and references therein.

[7] V. Rives and M. A. Ulibarri, *Coord. Chem. Rev.* **181**, 61 (1999), and references therein.

[8] C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.* **143**, 407 (1995), and references therein.

[9] I. V. Kozhevnikov, *Catal. Rev.* **37**, 311 (1995).

[10] I. V. Kozhevnikov, *Chem. Rev.* **98**, 171 (1998).

[11] N. Mizuno and M. Misono, *Chem. Rev.* **98**, 199 (1998).

[12] R. Newmann, *Prog. Inorg. Chem.* **47**, 317 (1998).

[13] T. Okuhara, N. Mizuno and M. Misono, *Adv. Catal.* **41**, 113 (1996).

[14] A. R. Siedle, C. G. Markell, P. A. Lyon, K. O. Hodgson and A. L. Roe, *Inorg. Chem.* **26**, 219 (1987).

[15] A. R. Siedle, R. A. Newmark, M. R. V. Sahyun, P. A. Lyon, S. L. Hunt and R. P. Skarjune, *J. Am. Chem. Soc.* **111**, 8346 (1989), and references therein.

[16] A. R. Siedle, W. B. Gleason, R. A. Newmark, R. P. Skarjune. P. A. Lyon. C. G. Markell, K. O. Hodgson and A. L. Roe, *Inorg. Chem.* **29**, 1667 (1990), and references therein.

[17] B. J. Hathaway, In: G. Wilkinson, R. D. Gillard and J. A. McCleverty (Eds.), *Comprehensive Coordination Chemistry* Vol. 5 (Pergamon Press, Oxford, 1987), p. 716.

[18] H. Mimoun, In: G. Wilkinson, R. D. Gillard and J. A. McCleverty (Eds.), *Comprehensive Coordination Chemistry* Vol. 6 (Pergamon Press, Oxford, 1987), p. 317.

[19] C. M. Tourné, G. F. Tourné, S. A. Malik and T. J. R. Weakley, *J. Inorg. Nucl. Chem.* **32**, 3875 (1970).

[20] J. A. Gamelas, F. A. S. Couto, M. C. N. Trovão, A. M. V. Cavaleiro, J. A. S. Cavaleiro and J. D. Pedrosa de Jesus, *Thermochim. Acta* **326**, 165 (1999).

[21] H. Nakai and Y. Deguchi, *Bull. Chem. Soc. Jpn.* **48**, 2557 (1975).

[22] B. J. Hathaway, I. M. Procter, R. C. Slade and A. A. G. Tomlinson, *J. Chem. Soc.* (*A*) p. 2219 (1969).

[23] W. D. Harrison, D. M. Kennedy, M. Power, R. Sheahan and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.* p. 1556 (1981).

[24] O. P. Anderson, *J. Chem. Soc. Dalton Trans.* p. 1237 (1973).

[25] A. Sedov, J. Kozisek, M. Kabesova, M. D. Jurco, J. Gazo and J. Garaj, *Inorg. Chim. Acta* **75**, 73 (1983).

[26] C. Niederhoffer, A. E. Martell, P. Rudolf and A. Clearfield, *Inorg. Chem.* **21**, 3734 (1982).

[27] H. R. Hunt, *J. Chem. Educ.* **54**, 710 (1977).

[28] C. Rocchiccioli-Deltcheff and R. Thouvenot, *J. Chem. Res.* (*S*) p. 46 (1977).

[29] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R. Thouvenot, *Inorg. Chem.* **22**, 207 (1983).

[30] J. S. Vaughan, C. T. O'Connor and C. Q. Fletcher, *J. Catal.* **147**, 441 (1994).

[31] R. D. Peacock and T. J. R. Weakley, *J. Chem. Soc.* (*A*) p. 1836 (1971).

[32] G. S. Chorgade and M. T. Pope, *J. Am. Chem. Soc.* **109**, 5134 (1987).

[33] R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini and M. Fournier, *Inorg. Chem.* **16**, 2916 (1977).

[34] T. J. R. Weakley, *J. Chem. Soc., Dalton Trans.* p. 341 (1973).

[35] G. Scholz, R. Lück, R. Stosser, H. J. Lunk and F. Ritschl, *J. Chem. Soc., Faraday Trans.* **87**, 717 (1991).

[36] J. A. Gamelas, I. C. Santos, C. Freire, B. Castro and A. M. V. Cavaleiro, *Polyhedron* **18**, 1163 (1999).

[37] M. Arakawa and T. Hirose, *J. Phys. Soc. Jpn.* **56**, 1178 (1987).

[38] B. J. Hathaway, In: G. Wilkinson, R. D. Gillard and J. A. McCleverty (Eds.), *Comprehensive Coordination Chemistry* Vol. 5 (Pergamon Press, Oxford, 1987), p. 533.

[39] D. E. De Vos, B. M. Weckhuysen and T. Bein, *J. Am. Chem. Soc.* **118**, 9615 (1996).

[40] T. Castner, G. S. Newell, W. C. Holton and C. P. Slichter, *J. Chem. Phys.* p. 668 (1960).

[41] H. W. Wijn and R. F. van Balderen, *J. Chem. Phys.* **46**, 1381 (1967).