Synthesis and Spectroscopic Studies of the Complexes of Ethylene-Bis (acetamide) with Some First Row Transition Metal Ions

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Summary: Synthesis of the complexes of ethylene-bis(acetamide) [EBA], formed with some first row transition metal salts are reported and have been characterized by their elemental analysis. The mode of coordination of the EBA ligand molecules in these complexes has been established by their FTIR spectra. The ESR spectra of the manganese (II) complexes consist of a broad band centered at $g_{eff} = 2$ region, suggesting very close to cubic symmetry at the Mn centres. The observed reflectance spectra values for the cobalt (II) and nickel (II) complexes also suggest octahedral structures for these complexes. When taken in conjunction with the X-ray crystal structure of $[Co(EBA)_2(H_2O)_2]Br_2$ and on the basis of their FTIR spectra, ESR spectra and electronic reflectance spectra, all these complexes are assigned octahedral structures, with ligand molecules coordinating with metal ions through their amide oxygen atoms.

Introduction

The first report on the effectiveness of polymethylene-bridged double ended bis(amides), of the type $CH_3CONH(CH_2)_n NHCOCH_3$ (n = 2-8), as inducers of erythroid differentiation in murine erythroleukemia cells [1] has prompted a need to study their interactions with metal ions. From the recent studies on the synthesis, spectroscopic as well as crystal structure studies of metal complexes of one of these bis(amides) i.e. hexamethylene-bisacetamide, $[CH_3CONH(CH_2)_6NHCOCH_3]$, it appears that the alkane-bridged double ended bis(amides) have appreciable propensity for linking metal ions and forming complexes [2-5]. Moreover, the very extensive capacity for variations in polymethylene-units, between the amide groups at two ends, should lead to a potentially rich and diverse range of complexes, particularly when taken into conjunction with differing favored modes of metal coordination geometries and the possible influences of changes in accompanying counter ions [6-7]. The crystal structure of one complex of ethylene-bis(acetamide) (EBA) has also been reported recently together with the synthesis of few of its complexes [7] but the synthesis and detailed spectroscopic studies of these complexes of ethylene-bis(acetamide) have not yet been carried out. I report here the synthesis of some new complexes of EBA, a detailed account of the method of preparation of those briefly reported previously [7] and the spectroscopic studies of these complexes of EBA, formed with some first row transition metal salts. Complexes of EBA, $[CH_3CONH(CH_2)_2 NHCOCH_3]$, with first row transition metal salts, synthesized in the present work include $Mn(EBA)Cl_2.2H_2O$, $Mn(EBA)_3Br_2.H_2O$, $Mn(EBA)_3(ClO_4)_2$, $Co(EBA)Cl_2.1.5H_2O$, $Co(EBA)_2Br_2.2H_2O$, $Co(EBA)_2(NO_3)_2.2H_2O$, $Co(EBA)_4(ClO_4)_2$, $Ni(EBA)Cl_2.2H_2O$, $Ni(EBA)_2Br_2.2H_2O$, $Ni(EBA)_2(NO_3)_2.3H_2O$ and $Ni(EBA)_3(ClO_4)_2.2.5H_2O$. All of these synthesized complexes have been characterized by their elemental analysis. The mode of coordination of EBA ligand molecules in these complexes has been established by their FTIR spectra. The electronic reflectance spectra and ESR spectra of these complexes have been measured to determine the coordination geometry of the metal ions in these synthesized complexes.

Results and Discussion

All the complexes of EBA with first row transition metal ions, studied in the present work, are summarized in Table- 1, together with their elemental analysis data.

FTIR Spectra

The characteristic bands in the FTIR spectra (4000 – 400 cm^{-1}) of these complexes of EBA with first row transition metal ions are listed in Table-2, together with the infra-red frequencies

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Table-1. Elemental analysis data for the complexes of EBA

Complex	% C Found (Calc.)	% H Found (Calc.)	% N Found (Calc.)
EBA	49.8 (50.0)	8.4 (8.3)	19.2 (19.4)
Mn (EBA)$Cl_2.2H_2O$	23.9 (23.6)	5.2 (5.2)	9.6 (9.2)
Mn $(EBA)_3Br_2.H_2O$	32.1 (32.5)	5.9 (5.8)	12.5 (12.6)
Mn $(EBA)_3(ClO_4)_2$	31.6 (31.5)	5.3 (5.3)	13.1 (12.3)
Co (EBA)$Cl_2.1.5H_2O$	23.9 (23.9)	5.3 (5.0)	9.5 (9.3)
Co $(EBA)_2Br_2.2H_2O$	27.0 (26.5)	5.2 (5.2)	10.7 (10.3)
Co $(EBA)_2(NO_3)_2.2H_2O$	28.5 (28.4)	5.6 (5.5)	16.6 (16.6)
Co $(EBA)_4(ClO_4)_2$	34.0 (34.5)	5.9 (5.8)	13.4 (13.4)
Ni (EBA)$Cl_2.2H_2O$	23.7 (23.3)	5.2 (5.2)	9.5 (9.1)
Ni $(EBA)_2Br_2.2H_2O$	25.9 (26.5)	5.2 (5.2)	10.3 (10.3)
Ni $(EBA)_2(NO_3)_2.3H_2O$	27.5 (27.4)	5.8 (5.7)	15.2 (16.0)
Ni $(EBA)_3(ClO_4)_2.2.5H_2O$	29.4 (29.4)	5.7 (5.6)	11.3 (11.4)

Table-2. FTIR spectra (4000 – 400 cm^{-1}) for the complexes of EBA

	(Amide I Band)	(Amide II Band)	(Amide III Band)
EBA	1658 VS	1562 VS	1288 S
Mn (EBA)$Cl_2.2H_2O$	1625 VS	1565 S	1303 S
Mn $(EBA)_3Br_2.H_2O$	1631 VS	1565 S 1546 S	1299 S
Mn $(EBA)_3(ClO_4)_2$	1656 S 1629 S	1554 S	1313 S 1288 M
Co (EBA)$Cl_2.1.5H_2O$	1623 S	1565 S	1305 S
Co $(EBA)_2Br_2.2H_2O$	1629 VS	1562 Sh 1542 S	1297 S
Co $(EBA)_2(NO_3)_2.2H_2O$	1631 S	1565 S	1303 S
Co $(EBA)_4(ClO_4)_2$	1673 S 1617 S	1579 Sh 1560 S	1297 S
Ni (EBA)$Cl_2.2H_2O$	1621 VS	1565 S	1303 S
Ni $(EBA)_2Br_2.2H_2O$	1625 VS	1562 S 1532 VS	1297 S
Ni $(EBA)_2(NO_3)_2.3H_2O$	1630 S	1564 S	1301 S
Ni $(EBA)_3(ClO_4)_2.2.5H_2O$	1673 Sh 1625 S	1556 S	1299 S

of the free ligand. The ligand molecules in all of these complexes are coordinated with the metal ions through their carbonyl oxygen atoms. The criterion for the existence of bonding through oxygen, in these complexes, is the shifting of the carbonyl stretching frequencies (amide I band) towards the lower frequency and of C-N stretching frequencies (amide III band) towards the higher frequency.

In the FTIR spectra of all these complexes, the frequency of carbonyl stretching vibrations i.e. amide I band (at 1658 cm^{-1} in the free ligand) decreases considerably on complex formation, indicating that the EBA molecules have been coordinated with the metal ions through their carbonyl oxygen atoms. Further, in the FTIR spectra of these complexes, the C-N stretching frequency i.e. amide III band (at 1288 cm^{-1} in the free ligand) appears at higher frequencies. All these band shifts, on complex formation, are consistent with a decreased C=O bond order and an increased C-N bond order.

In the FTIR spectra of all the perchlorate complexes i.e. Mn $(EBA)_3$ $(ClO_4)_2$, Co $(EBA)_4$ $(ClO_4)_2$ and Ni $(EBA)_3$ $(ClO_4)_2$. $2.5H_2O$, the carbonyl stretch i.e. amide I band, appeared as doublet, one band appearing at lower frequencies than the free ligand and the other appearing either at the same position or at higher frequencies than the free ligand. This splitting of amide I band suggests that not all the ligand molecules, in these perchlorate complexes, are behaving similarly and either some of the ligand molecules are monodentate, coordinating through one of the two amide carbonyl oxygen atoms or some of the EBA molecules are not coordinated and only hydrogen bonded.

Electron Spin Resonance Spectra

The X-band electron spin resonance (ESR) spectra of the manganese(II) complexes Mn(EBA)Cl_2. $2H_2O$, Mn $(EBA)_3$ $Br_2.H_2O$ and Mn$(EBA)_3$ $(ClO_4)_2$, in the solid state, are typical of a very close to octahedral coordination geometry at the manganese centres. In all these manganese (II) complexes the ESR spectra consist of a dominant, very strong broad band centered at g_{eff} = 2 region (Fig. 1), suggesting a coordination geometry very close to cubic symmetry. In the ESR spectra of

Table- 3. Reflectance spectra (30000 – 4000 cm^{-1}) for the complexes of EBA.

Complex	V_1 transition $[^4T_{2g}(F) \rightarrow {}^4T_{1g}(F)]$	V_2 transition $[^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)]$	V_3 transition $[^4T_{1g}(P) \rightarrow {}^4T_{1g}(F)]$
Co (EBA)Cl_2.1.5H_2O	7800	15900 S	18800 Sh, 19600 VS
Co (EBA)$_2Br_2$.2H_2O	7500	14600 S	19300 VS, 21350 Sh
Co (EBA)$_2(NO_3)_2$.2H_2O	7850	14300 W	19150 VS, 21050 Sh
Co (EBA)$_4(ClO_4)_2$	7200	14500 W	19000 VS, 20700 Sh
	$[^1T_{2g}(F) \rightarrow {}^3A_{2g}(F)]$	$[^1T_{1g}(F) \rightarrow {}^3A_{2g}(F)]$	$[^1T_{1g}(P) \rightarrow {}^3A_{2g}(F)]$
Ni (EBA)Cl_2.2H_2O	7050	12500	23000
Ni (EBA)$_2Br_2$.2H_2O	8500	13700	24400
Ni (EBA)$_2(NO_3)_2$.3H_2O	8500	13700	24700

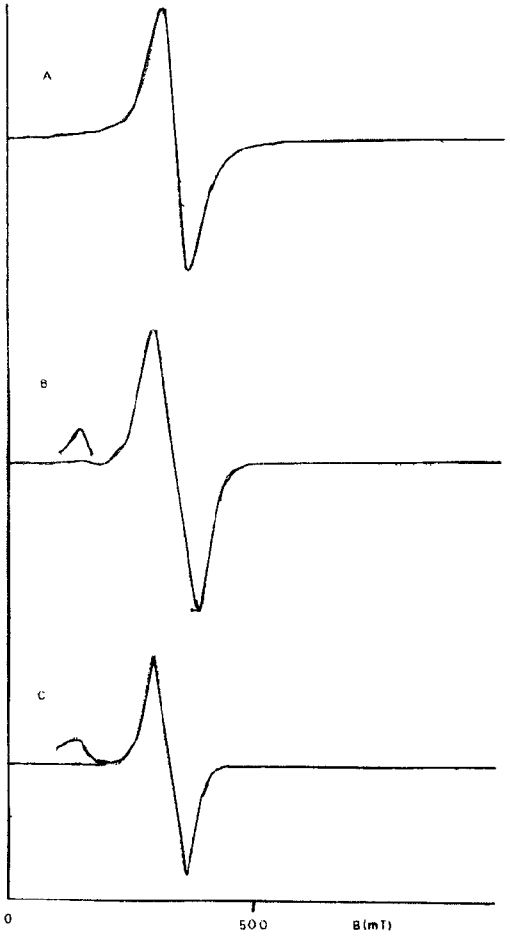

Fig. 1. X-band ESR spectra of
(A) Mn(EBA)Cl_2.2H_2O
(B) Mn(EBA)$_3Br_2$.H_2O
(C) Mn(EBA)$_3(ClO_4)_2$

Mn(EBA)$_3Br_2$.H_2O and Mn(EBA)$_3(ClO_4)_2$, a second, very weak band appeared at 148.0 and 152.2 mT (Fig. 1) suggesting very small departure from strict octahedral structures for them.

Electronic Reflectance Spectra

The electronic reflectance spectra of all the complexes of cobalt (II) and nickel (II), synthesized in the present work, were measured in the solid state over the range from 4000 cm^{-1} to 30000 cm^{-1}. The characteristic absorption bands observed in the reflectance spectra of these complexes are listed in Table-3 and shown in Figs. 2-4.

The reflectance spectra of all the cobalt(II) complexes i.e. Co (EBA)Cl_2.1.5H_2O, Co (EBA)$_2Br_2$. 2H_2O, Co (EBA)$_2$ $(NO_3)_2$. 2H_2O and Co(EBA)$_3$ $(ClO_4)_2$ suggest the presence of an essentially octahedral cobalt coordination geometry for these complexes. In $CoCl_2$, $CoBr_2$, $Co(NO_3)_2$ and $Co(ClO_4)_2$ complexes a band appears around 7800, 7500, 7850 and 7200 cm^{-1} respectively, which is assigned to the V_1 transition [$^4T_{2g}$ (F) → $^4T_{1g}$ (F)], of an essentially octahedral chromophore. The V_3 transition [$^4T_{1g}$ (P) → $^4T_{1g}$ (F)], in octahedral cobalt (II) complexes appears around 20000 cm^{-1}. In $CoCl_2$ complex this band appears at 19600 cm^{-1} together with a shoulder at ca. 18800 cm^{-1} and in $CoBr_2$ complex this band was seen at 19300 cm^{-1} with a shoulder at ca. 21350 cm^{-1}. Similarly in $Co(NO_3)_2$ complex the V_3 transition appeared, as a very strong band, at 19150 cm^{-1} together with a shoulder at ca. 21050 cm^{-1} and in $Co(ClO_4)_2$ complex this band appears as a very strong band at 19000 cm^{-1} and a shoulder at around 20700 cm^{-1}. The V_2 transition [$^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$], in octahedral cobalt(II) complexes is often very weak appearing as a shoulder [11]. In $Co(NO_3)_2$ and $Co(ClO_4)_2$ complexes this weak V_2 transition appears at 14300 and 14500 cm^{-1} respectively (Fig. 2). In contrast to nitrate and perchlorate complexes, this V_2 transition in $CoCl_2$ and $CoBr_2$ complexes appears with great intensity at 15900 and 14600 cm^{-1} respectively (Fig. 3).

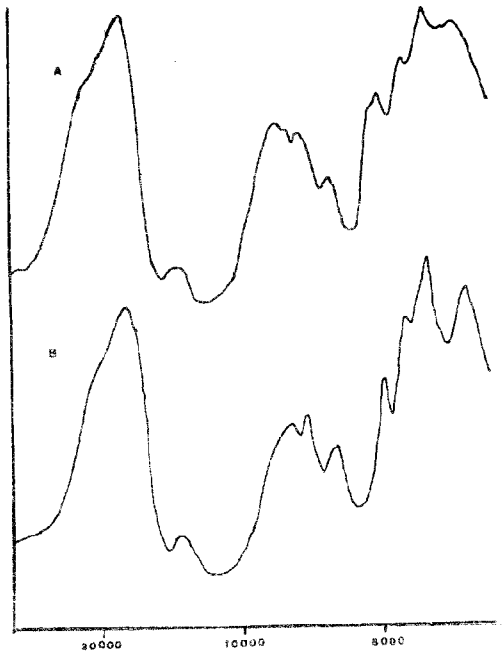

Fig. 2. Reflectance spectra of
(A) $Co(EBA)_2(NO_3)_2.2H_2O$
(B) $Co(EBA)_2(ClO_4)_2$

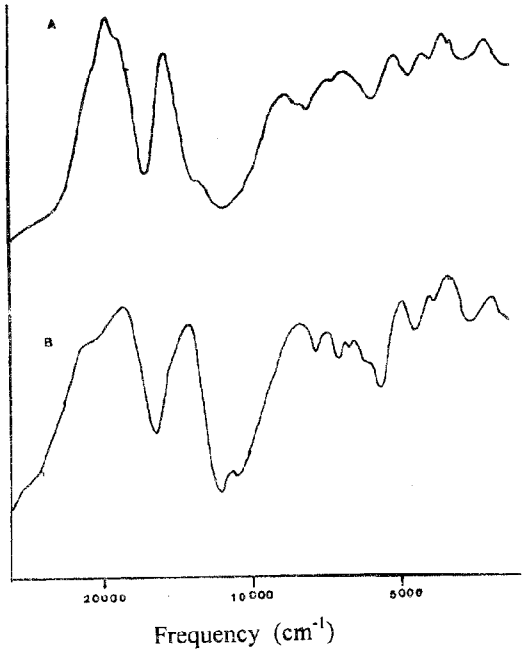

Fig. 3. Reflectance spectra of
(A) $Co(EBA)Cl_2.1.5H_2O$
(B) $Co(EBA)_2Br_2.2H_2O$

As with the corresponding cobalt (II) complexes, the reflectance spectra of the nickel (II) complexes i.e. Ni $(EBA)Cl_2.2H_2O$, Ni $(EBA)_2Br_2.2H_2O$ and Ni $(EBA)_2(NO_3)_2.3H_2O$ suggest essentially octahedral structures for these complexes [Fig. 4]. The very strong band centered at 23000, 24400 and 24700 cm^{-1} in $NiCl_2$, $NiBr_2$ and $Ni(NO_3)_2$ complexes respectively is assigned to the V_3 transition $[^3T_{1g}(P) \rightarrow {}^3A_{2g}(F)]$, of octahedral coordination geometry. Similarly, a second strong band at 12500, 13700 and 13700 cm^{-1} respectively, in these complexes, is essentially assigned to the V_2 transition $[^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)]$, of O_h symmetry. The third medium intensity absorption centered at 7050, 8500 and 8500 cm^{-1}, observed in the reflectance spectra of $NiCl_2$, $NiBr_2$ and $Ni(NO_3)_2$ complexes respectively, undoubtedly arises from the V_1 transition $[^3T_{2g}(F) \rightarrow {}^3A_{2g}(F)]$ of octahedral geometry. However, this V_1 transition, in these nickel (II) complexes, appears as a broad band because of the ligand overtone and combination vibrational bands which appear in this region (Fig. 4). Further, the observed reflectance

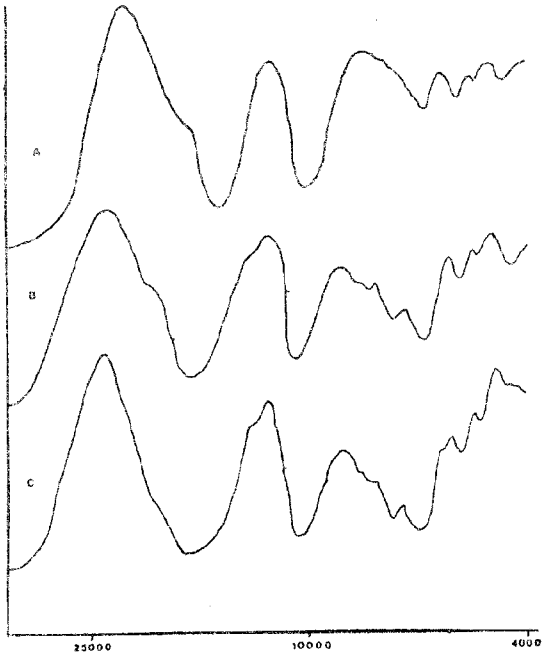

Fig. 4. Reflectance spectra of
(A) $Ni(EBA)Cl_2.2H_2O$
(B) $Ni(EBA)_2Br_2.2H_2O$
(C) $Ni(EBA)_2(NO_3)_2.3H_2O$

spectra values, for these complexes, agree nicely with a slightly lower ligand field strength for EBA ligand than for nickel (II) hexaaqua ion [10] and resemble closely with those reported previously for octahedral Ni (II) complexes [6, 11-12], confirming that all of these complexes also have the octahedral nickel coordination geometry.

When taken in conjunction with the X-ray crystal structure of $[Co(EBA)_2(H_2O)_2]$ Br_2 [7] and on the basis of their F.T.I.R. spectra, ESR spectra of manganese (II) complexes and the reflectance spectra of corresponding cobalt (II) and nickel (II) complexes, these results suggest that all of these complexes of EBA, synthesized in the present work, posses octahedral structures at the metal centres.

Experimental

Preparation of Complexes

All the chemicals used in the present work were pure analytical grade and were used without further purification.

Ethylene-bis(acetamide) (EBA)

This compound was prepared by the method used previously [1].

$Mn(EBA)Cl_2.2H_2O$

A hot solution of $MnCl_2.4H_2O$ (0.1 mmol) in a mixture of acetonitrile (5 cm^3) and methanol (2 cm^3) was mixed with a hot solution of EBA (0.2 mmol) in acetonitrile (5 cm^3). Boiled the resultant solution, filtered and allowed to stand. White crystalline solid formed on cooling was collected and dried in *vacuo*

$Mn(EBA)_3Br_2.H_2O$

$MnBr_2.4H_2O$ (0.1 mmol) was dissolved in a mixture of acetonitrile (5 cm^3) and 2, 2-dimethoxypropane (1 cm^3) and mixed with a solution of EBA (0.2 mmol) in acetonitrile (5 cm^3). White crystals settled down in 3 hours time.

$Mn(EBA)_3(ClO_4)_2$.

A warm solution of EBA (0.3 mmol) in acetonitrile (5 cm^3) was added to a solution of manganese (II) perchlorate hexahydrate (0.1 mmol) in methanol (1 cm^3). The oily product thus formed gave white precipitates on triturating with diethyl ether.

$Co(EBA)Cl_2.1.5H_2O$

Dissolved cobalt (II) chloride hexahydrate (0.1 mmol) in acetonitrile (5 cm^3) and mixed with the similar solution of EBA (0.2 mmol) in acetonitrile (5 cm^3). Boiled and allowed to stand for slow evaporation. The crystals were formed in 3 days time.

$Co(EBA)_2Br_2\ 2H_2O$

A hot solution of hydrated cobalt (II) bromide (0.1 mmol) in a mixture of acetonitrile (5 cm^3) and 2,2-dimethoxypropane (1 cm^3) was mixed with a hot solution of EBA (0.2 mmol) in acetonitrile (5 cm^3). The resultant solution was boiled, filtered and allowed to stand. Pink crystals appeared in 4 days time which were collected and dried.

$Co(EBA)_2(NO_3)_2.2H_2O$

Mixing a hot solution of $Co(NO_3)_2.6H_2O$ (0.1 mmol) in methanol (1 cm^3) with a hot solution of EBA (0.2 mmol) in acetonitrile (5 cm^3) resulted in the formation of oily product which was converted to fine pink powder on triturating with diethyl ether.

$Co(EBA)_4(ClO_4)_2$

$Co(ClO_4)_2.\ 6H_2O$ (0.1 mmol) was dissolved in a mixture of hot methanol (4 cm^3) and 2,2-dimethoxypropane (1 cm^3) and mixed with a hot solution of EBA (0.3 mmol) in methanol (5 cm^3). On complete evaporation the pink powder was obtained on triturating with diethyl ether.

$Ni(EBA)Cl_2.2H_2O$

Dissolved $NiCl_2.6H_2O$ (0.1 mmol) in a mixture of acetonitrile (5 cm^3) and methanol (2 cm^3) and mixed with the hot solution of EBA (0.2 mmol) in acetonitrile (5 cm^3). Boiled the resulting solution and placed for evaporation. The yellow crystals thus formed were washed with diethyl ether and dried in *vacuo*.

$Ni(EBA)_2Br_2.2H_2O$

This complex was prepared by slow concentration of a solution of hydrated nickel (II) bromide (0.1 mmol) and EBA (0.2 mmol) in a mixture of acetonitrile (10 cm^3) and 2, 2-dimethoxypropane (1 cm^3). Green crystals thus formed were collected, washed with diethyl ether and dried in *vacuo*.

$Ni(EBA)_2(NO_3)_2.3H_2O$

Mixing a hot solution of nickel (II) nitrate hexahydrate (0.1 mmol) in methanol (1 cm^3) with a hot solution of EBA (0.2 mmol) in acetonitrile (5 cm^3) resulted in the formation of oily product which was converted to fine green powder on triturating with diethyl ether.

$Ni(EBA)_3(ClO_4)_2.2.5H_2O$

This complex was prepared by the similar method used for the preparation of corresponding manganese complex. The green precipitates formed were washed with diethyl ether and dried in *vacuo*.

Analysis for % age composition of C, H and N were carried out by the Scientific Analysis and Consultancy Service, University of North London, UK.

FTIR spectra (4000-400 cm^{-1}) were obtained by using Perkin-Elmer 1720 FTIR spectrometer.

X-band ESR spectra were obtained using a Varian E 12 spectrometer, on powdered solid samples at room temperature.

Diffuse reflectance spectra of the powder samples, over the range 18500-4000 cm^{-1}, were obtained on Beckman DK 2 spectrometer and for the range 30000-12000 cm^{-1} on a Pye Unicam SP8-100 spectrometer.

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