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Synthesis and characterization of some transition metals polymer complexes

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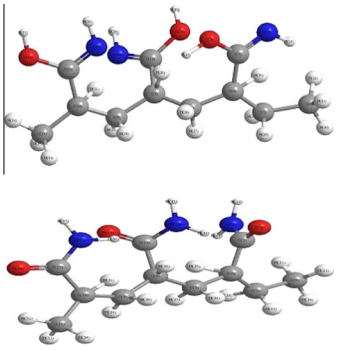
HIGHLIGHTS

- Co^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+} and Fe^{3+} complexes of polyacrylamide were prepared.
- The six polymer complexes were characterized by different measurements.
- Some applications of polyacrylamide were done.

GRAPHICAL ABSTRACT



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ABSTRACT

Co^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+} and Fe^{3+} complexes of Polyacrylamide are prepared and characterized by elemental analyses, IR, UV–Vis spectra, magnetic measurements, and thermal analyses. The data suggests octahedral geometry for all complexes. The thermal behavior of the complexes has been studied applying TG, DTA, and DSC techniques, and the thermodynamic parameters and mechanisms of the decompositions were evaluated. The $\Delta S\#$ values of the decomposition steps of the metal complexes indicated that the activated fragments have more ordered structure than the undecomposed complexes. The thermal processes proceeded in complicated mechanisms where the bond between the central metal ion and the ligands dissociates after losing $6(C_2H_5N)$ and 6(CO), the metal complexes are ended with metal as a final product. Viscosity and Shale instability using liner swell meter were carried out. Comparisons of the experimental and theoretical IR spectra were also carried out besides some other theoretical calculations.

Introduction

Study of the polymer–metal complexes has received increased interest in various branches of chemistry, chemical technology and biology and the subject has been reviewed periodically [1–4]. The chelating polymers find applications in collecting transition metal ions as well as alkali and alkaline earth metal ion separation [5] preconcentration and recovery of trace metal ions [6], catalysis [7,8], organic synthesis [9,10], nuclear chemistry [11], water and waste water-treatment [12,13], pollution control [14], industrial processes [15], hydrometallurgy [16,17] and polymer drug graft [18]. In addition polymer–metal complexes are also used as mechanochemical system and as models of bioinorganic systems [19,20].

Polyacrylamides are a class of polymers formed from acrylamide alone or copolymerized with other monomers. Polyacrylamides have been used in a variety of applications, soil conditioning to reduce soil erosion, agriculture, oil recovery, biomedical applications and have been used in water treatment

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to improve the process of sludge thickening and dewatering as flocculants or coagulants in the highest volume among all the polymer types. In potable water treatment processes, polyacrylamides are often exposed to oxidants (e.g. chlorine and permanganate) and UV irradiation from sunlight or artificial sources.

Other uses include mixing with pesticides as a thickening agent and as a medium for hydroponically grown crops, in sugar refining [21], and as a binder of bone cement [22]. Although there are numerous work on complexation of different polymers with transition metal [23,24], only Ni^{2+} complex of polyacrylamide was prepared and characterized [25].

Experimental

Preparation of metal complexes

The complexation of the resins were investigated toward $CoSO_4$, $NiSO_4$, $CuCl_2$, $CrCl_3$, $MnCl_2$ and $FeCl_3$ at their neutral pH. In all the complexation studies, one gm of metals salt dissolved in 100 ml distilled water were added to one gm of polymeric ligand dissolved in 100 ml distilled water, the metal salt solution was mixed with the ligand solution, the reaction mixture was stirred for 2 h. The complexed resins were collected by filtration, washed with distilled water and dried in a vacuum desiccators anhydrous $CaCl_2$.

Physical measurements

Elemental analyses C, H, N contents of the synthesized complexes were analyzed by the usual method with the aid of CHN analyzer. Metal analysis for Co^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, Mn^{2+} and Fe^{3+} were analyzed by complexometerically by EDTA titration [26]. Table 1 shows the analytical results for the polymer ligand itself and its complexes. The KBr IR spectra of ligand and the six complexes were recorded on a Perkin–Elmer spectrophotometer covering the frequency range 4000–200 cm^{-1}. X-band electron spin resonance spectra were recorded for Copper polymer complex only with a reflection spectrometer operating at (9.1–9.8) GHz in a cylindrical resonance cavity with 100 kHz modulation. The *g*-values were determined by comparison with DPPH (diphenyl picryl hydrazide) signal, the control field of the standard (DPPH) is 3300 G. The UV–Vis spectra of the solid complexes were measured in Nujol mull spectra [27]. Molar magnetic susceptibilities, corrected for diamagnetism using Pascal's constants were determined at lab temperature (298 K). The instrument was calibrated with Hg[Co(SCN)]. The magnetic moment values were evaluated at room temperature using a Sherwood scientific magnetic susceptibility balance. Differential thermal analysis (DTA), differential scanning calorimetric (DSC) and thermogravimetry analysis (TG) of solid complexes were carried out using a shimadzu DTA/TG-50. The rate of heating was 10 °C min^{-1}. The cell used was platinum, and the atmospheric nitrogen rate flow was 20 mL min^{-1}. The viscosity was carried out using a FANN VG meter Model 35 Viscometer and Brookfield HBDV-II + PRO Digital Programmable Viscometer. Shale instability was carried out using a Linear Swell Meter LSM 2000. Comparisons of the experimental and theoretical IR spectra were carried out besides some other theoretical calculations.

Table 1
Analytical and physical properties of the ligand and its metal complexes[a].

Sample	Color	Calculated/(found) (%)			
		C (%)	H (%)	N (%)	M (%)
PACM	White	50.7 (50.4)	7.04 (7.0)	22.54 (22.2)	–
$[Cu(ACM)_6]_n$	Blue	45.23 (45.2)	3.77 (3.4)	17.59 (17.0)	13.31 (13.04)
$[Cr(ACM)_6]_n$	Green	46.35 (46.0)	3.86 (3.7)	18.03 (17.4)	11.16 (11.01)
$[Co(ACM)_6]_n$	Pink	45.67 (45.5)	3.81 (3.8)	17.76 (17.1)	12.46 (12.08)
$[Fe(ACM)_6]_n$	Reddish brown	45.97 (45.7)	3.83 (3.7)	17.88 (17.1)	11.89 (11.52)
$[NI(ACM)_6]_n$	Pale green	45.70 (45.7)	3.80 (3.7)	17.77 (17.0)	12.42 (12.22)
$[Mn(ACM)_6]_n$	Buff	46.06 (46.0)	3.84 (3.8)	17.91 (17.1)	11.72 (11.61)

[a] All the complexes are with melting point >300 °C, however that of the ligand is 250 °C.

Results and discussion

Infrared spectroscopy

The ν CH_2, ν NH and ν CN of the ligand (Table 2) are of minor importance for complexation. Meanwhile, the ν C=O is of major importance for complexation followed by ν NH_2 to a less extent. The ν C=O band position of PACM ligand at 1642 cm^{-1} [29] is changed on complexation with Cu(II), Ni(II), Cr(III), Fe(III), Co(II) and Mn(II) polymer complexes indicating its participation in complex formation. The ν NH_2 band position of PACM ligand at 3440 cm^{-1} [29] is changed on complexation with Cu(II), Ni(II), Cr(III), Fe(III), Co(II) and Mn(II) indicating its participation in complex formation [30–32]. As a result of IR and elemental analyses results, the structure of the complexes may have octahedral geometry containing the metal coordinated to both nitrogen and oxygen atoms via resonance, Structure 1.

According to Mukhles Sowwan et al. Ni^{2+}–complex of polyacrylamide shows that polyacrylamide act as monodentate ligand through nitrogen atom of NH_2 group [25].

Theoretical vibrational analysis of PACM

PACM contains amide group (H_2N=C=O) can exist as keto or enol form through tautomerism of mobile hydrogen atom depending on moving atom one site (N atom) to another (O atom) in order to acquire the spectroscopic nature of PACM molecule, the frequency calculation analysis [33,34], was made for free polymer molecule consists of three monomer units for both keto and enol forms, while experimental spectrum was performed for solid sample. It seems that there are small differences between theoretical and experimental vibrational wave numbers [35], (Fig. 1). The band appears at 3440 cm^{-1} in the experimental IR does not appear in theoretical keto form but appear in the theoretical enol form at 3509 cm^{-1} confirming the existence of both keto and enol forms. The correlation graphic described harmony between the theoretical wave numbers (Fig. 1). The relations between the calculated and experimental wave numbers are linear and described by the following equations:

For the keto form υ_{cal}

$$= 0.993\upsilon_{exp} + 12.47 \text{ with correlation coefficients } (R^2 = 0.997)$$

Table 2
Fundamental infrared bands (cm^{-1}) of PACM and its complexes.

Compound	ν (cm^{-1}) NH_2	ν (cm^{-1}) $CH_{2(s)}$	ν (cm^{-1}) C=O	ν (cm^{-1}) N–H	ν (cm^{-1}) C–N
PACM	3440	2925	1642	–	1453
$[Cu(ACM)_6]_n$	3447	2925	1648	1326	1453
$[Ni(ACM)_6]_n$	3442	2926	1657	1323	1450
$[Cr\ (ACM)_6]_n$	3444	2927	1649	1326	1453
$[Fe(ACM)_6]_n$	3443	2927	1664	1325	1453
$[Co(ACM)_6]_n$	3442	2926	1650	1326	1453
$[Mn(ACM)_6]_n$	3442	2927	1662	1324	1451