

XRD and optical microscopic studies of Co(III) complexes containing 5-cyano-6-(4-pyridyl)-2-thiouracil, thymine and adenine bases

LALLAN MISHRA*, BRAJESH PATHAK and R K MANDAL[†]

Department of Chemistry, [†]Department of Metallurgical Engineering, Banaras Hindu University, Varanasi 221 005, India

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Abstract. Multifunctional ligand 5-cyano-6-(4-pyridyl)-2-thiouracil (L) was prepared and allowed to react with *trans* [Co(en)₂Cl₂]⁺Cl⁻ resulting into [Co(en)₂LCl]²⁺·2Cl⁻ which upon further reaction with equimolar ratio of ligand [L] gave the complex [Co(en)₂L₂]³⁺·3Cl⁻. These metal complexes were then separately reacted with thymine and adenine bases. Complexes thus prepared after characterization by their elemental analysis, FAB mass and spectral (IR, ¹HNMR, UV-visible) data were studied for their powder X-ray diffraction and optical microscopic characteristics.

Keywords. Supramolecular; hydrogen-bonding; thymine; adenine.

1. Introduction

Self-assembly of molecules containing complementary hydrogen-bonding groups structurally related to those found in nucleotide bases are of current research interest in the area of supramolecular chemistry (Burrows *et al* 1995). Since non-covalent interactions play a special role in supramolecular chemistry (Lehn 1988, 1990), various supramolecular species have been synthesized by adopting the procedure of non-covalently assisted synthetic technique which primarily relies on the principle of stabilization provided by the interaction between recognition site incorporated within precursors (Muller-Dethlefs and Hobza 2000). In this context, the development of multifunctional ligand leading to the formation of the metal complexes capable of recognizing nucleotide bases by means of hydrogen-bonding have been considered quite promising. Metal based supramolecular complexes have also been used for inducing the formation of supramolecular mesophase and self-assembled nanostructure (Burrows *et al* 1995). Additionally, rhodium acetate dimer and related complexes have shown good antitumour activity (Clarke *et al* 1999), so cobalt being congener of rhodium was thought to be of great biological relevance.

Thus on the basis of above reports it was considered worthwhile to synthesize some Co(III) complexes bearing multifunctional ligand (L) scheme 1 and to attach them with adenine and thymine bases for their solid states structural studies using X-ray powder diffraction and optical microscopy techniques.

2. Experimental

5-Cyano-6-(4-pyridyl)-2-thiouracil (L) and *trans* [Co(en)₂Cl₂]⁺Cl⁻ were prepared by the reported procedures of Upadhyay and Ram (1999) and Haworth and Elsen (1974) respectively.

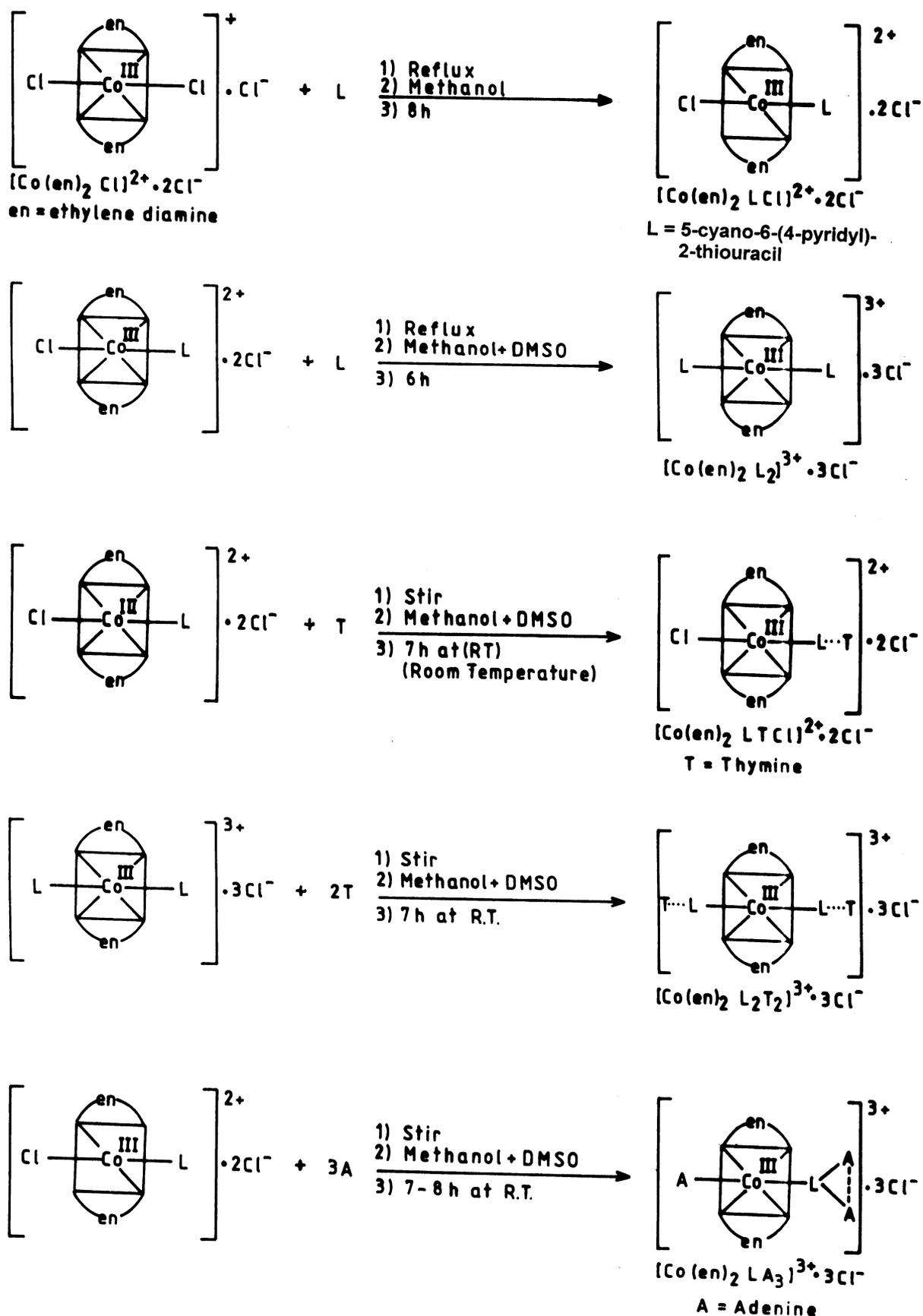
Synthetic strategy reported by Mishra *et al* (2001) is shown in scheme 1. In this procedure, equimolar ratio of L and [Co(en)₂Cl₂]⁺Cl⁻ were allowed to react in methanol (~ 10 ml) which gave the initial product identified as [Co(en)₂LCl]²⁺·2Cl⁻ which upon further reaction with equimolar ratio (1 : 1) of L in methanol containing few drops of DMSO gave another product identified as [Co(en)₂L₂]³⁺·3Cl⁻. These complexes were then further allowed to react separately with 1 : 1 and 1 : 2 molar ratio of thymine, however 1 : 3 molar ratio of the complexes [Co(en)₂LCl]²⁺·2Cl⁻ and adenine in similar condition yielded the complex [Co(en)₂LA₃]³⁺·3Cl⁻.

3. Results and discussion

Details of the instruments used for spectral (IR, UV-visible, ¹HNMR) studies have already been reported elsewhere (Mishra *et al* 2001), however, powder X-ray diffraction data were collected on PW1717 and optical microscopic study was done using Leitz optical microscope.

Synthetic strategy of the complexes as shown in scheme 1 indicated the different types of the complexes used in present study. The composition of the complexes has been assigned on the basis elemental analysis and FAB mass data (Mishra *et al* 2001). Complexes were found to decompose after heating above room temperature. The structure of the complexes, are however, supported by their spectroscopic data.

*Author for correspondence



Scheme 1. Synthetic strategy adopted for the preparation of the complexes.

From the IR spectra of the complexes peaks observed at 1610 cm^{-1} indicated the coordination of pyridyl group. However, lowering of the ligand peaks (1680 , 3150 and 1125 cm^{-1}) by $5\text{--}10\text{ cm}^{-1}$ was observed in the spectra of its complexes. Similarly lowering in --NH and >C=O vibration of thymine and adenine in the spectra of the complexes supported their interaction with the ligand. However, $\text{n C}\equiv\text{N}$ (2210 cm^{-1}) of the ligand remained constant in the spectra of the complexes. Furthermore, the presence of thymine and adenine in the corresponding complexes was also supported by the observation of --NH and --NH_2 protons at δ 10.6 and 7.3 ppm respectively in their $^1\text{H NMR}$ spectra.

From the visible spectrum of the complex, $[\text{Co}(\text{en})_2\text{LCI}]^{2+}\cdot 2\text{Cl}^-$ transitions observed at 480 and 504 nm were assigned to $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ respectively (Cotton *et al* 1999). The transition at lower energy (504 nm) was found to be split showing its *trans* configuration. However, red shift by $8\text{--}16\text{ nm}$ was observed in the spectra of the complexes.

Thus these spectral studies supported the structure of the complexes as shown in scheme 1.

3.1 XRD studies

Calculated and experimental d values (d_{cal}), (d_{obs}), for the representative complex $[\text{Co}(\text{en})_2\text{LTCI}]^{2+}\cdot 2\text{Cl}^-$ are presented in table 1 together with their lattice parameters calculated by Ito's method (Azaroff and Buerger 1958). Majority of the X-ray powder diffraction peaks have been indexed by the crystal system having lattice parameters indicated in table 2. It has been noted from this table that all

complexes except $[\text{Co}(\text{en})_2\text{LCI}]^{2+}\cdot 2\text{Cl}^-$ displayed orthorhombic crystal systems whereas $[\text{Co}(\text{en})_2\text{LCI}]^{2+}\cdot 2\text{Cl}^-$ has tetragonal system. Root means square deviation of d values (R) (Cullity 1978) for these systems are also shown in table 2. The low value of R for some of the complexes supported that the coherently scattering domain size (t) (Cullity 1978) are large, though lie well below to that expected for normal size ($> 1000\text{ \AA}$) of crystallites. For $[\text{Co}(\text{en})_2\text{LCI}]^{2+}\cdot 2\text{Cl}^-$ in particular, this size is $\sim 10\text{ nm}$ and may be behaving like a nanocrystalline complex having large volume fractions of homophase or heterophase boundaries, however, we could not comment on the nature of above interfaces as it require high resolution electron microscopic studies. We may conclude this discussion by stating that $[\text{Co}(\text{en})_2\text{LCI}]^{2+}\cdot 2\text{Cl}^-$ will have lot of structural defects *vis-à-vis* those of $[\text{Co}(\text{en})_2\text{LTCI}]^{2+}\cdot 2\text{Cl}^-$ and $[\text{Co}(\text{en})_2\text{L}_2\text{T}_2]^{3+}\cdot 3\text{Cl}^-$ where the t values are relatively larger. We have made this statement owing to the fact that property of these complexes in the solid state will be dependent on such defects as is true for many other class of materials.

The change in the crystal structure from tetragonal to orthorhombic for $[\text{Co}(\text{en})_2\text{LCI}]^{2+}\cdot 2\text{Cl}^-$ and $[\text{Co}(\text{en})_2\text{L}_2]^{3+}\cdot 3\text{Cl}^-$ can be understood by recalling that number of ligands in $[\text{Co}(\text{en})_2\text{L}_2]^{3+}\cdot 3\text{Cl}^-$ impart a more symmetric configuration through covalent bonding hence reducing the unit cell volume (lattice parameters in table 2). Furthermore, complexes other than the above displayed orthorhombic structures which could be attributed to the presence of weaker bonding (hydrogen-bonding) in them. We have invariably noticed that the peak widths in almost all the cases were higher than those introduced by instrumental broadening in XRD data which clearly indicated

Table 1. XRD data for a representative complex $[\text{Co}(\text{en})_2\text{TCl}]^{2+}\cdot 2\text{Cl}^-$, $I \sim 1.54\text{ \AA}$.

Angle (2θ)	d value (\AA)	$1/d^2$ (obs.)	$1/d^2$ (calcd.)	hkl
6.720	13.1429	0.0057	0.0057	100
8.755	10.0920	0.0098	0.0098	010
13.535	6.5368	0.0234	0.0234	001
15.020	5.8937	0.0287	0.0291	101
20.990	4.2289	0.0559	0.0563	211
22.100	4.0190	0.0619	0.0619	310
26.590	3.3496	0.0891	0.0883	030
26.940	3.3069	0.0914	0.0913	320
29.495	3.0260	0.1092	0.1091	112
30.685	2.9113	0.1172	0.1174	131
32.265	2.7723	0.1301	0.1318	420
33.450	2.6767	0.1395	0.1385	122
42.960	2.1036	0.2259	0.2254	422
43.540	2.0769	0.2318	0.2318	601
44.510	2.0339	0.2417	0.2416	611
47.405	1.9162	0.2723	0.2730	441
50.855	1.7940	0.3107	0.3118	612
55.155	1.6639	0.3611	0.3621	152
58.385	1.5793	0.4009	0.3999	261

size restriction on the coherently scattering domain. This is a characteristic which is true for all the complexes with large motifs. As such, systems would require more idealized condition of growth for producing defects free grains.

3.2 Microstructural characterization

Figures 1a and b depict the optical micrographs of a representative section of $[\text{Co}(\text{en})_2\text{LCl}]^{2+}\cdot 2\text{Cl}^-$ and $[\text{Co}(\text{en})_2\text{L}_2]^{3+}\cdot 3\text{Cl}^-$ specimen in the form of a pellet of identical diameter (1 cm) and thickness $\sim 1\text{--}3$ mm. The usual technique for the preparation of surfaces for optical micrography has been adopted. We noted that there is a uniform matrix of $[\text{Co}(\text{en})_2\text{LCl}]^{2+}\cdot 2\text{Cl}^-$ over which smaller regions separated by a black-contrast from the background could be seen. This leads us to believe that we are dealing with two-phase material. It is to be remembered that some of the XRD peaks for this case could not be indexed based on tetragonal cell parameters (cf. 3.1). By taking these two observations into account we may assume that this minor phase dispersed over the regions (figure 1a) may be due to the formation of $[\text{Co}(\text{en})_2\text{L}_2]^{3+}\cdot 3\text{Cl}^-$ in the system. However, in contrast to the above, a single phase formation of $[\text{Co}(\text{en})_2\text{L}_2]^{3+}\cdot 3\text{Cl}^-$ complex having rod morphologies in the form of a bundle is displayed (figure 1b). The orientation of this rod bundles are different which is clearly depicted in figure

1c. We further observed a centre marked as 'A' on the micrograph from where different branches are coming out. The smaller diameter of the rod is $\sim 1\ \mu\text{m}$ whereas the larger one has $\sim 3\ \mu\text{m}$ and the uniform morphologies throughout the specimen (figures 1b–c), prove our point of formation of a single phase and supports the reliability of our indexing proposal based on the orthorhombic system of given parameters.

Furthermore, addition of a drop of acetone to one side of the pellet of $[\text{Co}(\text{en})_2\text{L}_2]^{3+}\cdot 3\text{Cl}^-$, brings changes in the morphologies of the above systems and is shown in figure 1d. This micrograph also depicts the interface between the rod bundle morphologies and those after treatment with acetone. This may happen owing to the attachment of acetone to systems most likely through hydrogen bonding. This statement could be substantiated by making comparison of the acetone treated $[\text{Co}(\text{en})_2\text{L}_2]^{3+}\cdot 3\text{Cl}^-$ specimen with that of $[\text{Co}(\text{en})_2\text{L}_2\text{T}_2]^{3+}\cdot 3\text{Cl}^-$ (figure 1e). The attachment of acetone with the ligand is quite possible as it possesses the groups like $>\text{C}=\text{O}$ needed for bonding with the complementary group present in the ligand system.

Upon comparison of optical micrographs of $[\text{Co}(\text{en})_2\text{LTCl}]^{2+}\cdot 2\text{Cl}^-$ (figure 1f) and $[\text{Co}(\text{en})_2\text{LA}_3]^{3+}\cdot 3\text{Cl}^-$ (figure 1g) with that of starting compound $[\text{Co}(\text{en})_2\text{LCl}]^{2+}\cdot 2\text{Cl}^-$, network morphologies could be seen in above systems and the features are totally different from those seen in $[\text{Co}(\text{en})_2\text{LCl}]^{2+}\cdot 2\text{Cl}^-$ (figure 1a). This supports the formation of single phase in system $[\text{Co}(\text{en})_2\text{LTCl}]^{2+}\cdot 2\text{Cl}^-$.

Table 2. Lattice parameters of the complexes.

Complexes	Root mean square deviation of d values (' R ')	Crystal system and lattice parameter (\AA)	q (angle at maximum intensity for the phase)	b (half width at half maximum $\times 10^{-3}$ in radian)	t (coherently scattering domain size) in \AA
$[\text{Co}(\text{en})_2\text{LCl}]^{2+}\cdot 2\text{Cl}^-$	6.3	Tetragonal $a = 10.19$ $b = 10.19$ $c = 6.01$	4.3	13.7	101
$[\text{Co}(\text{en})_2\text{L}_2]^{3+}\cdot 3\text{Cl}^-$	7.7	Orthorhombic $a = 10.21$ $b = 7.80$ $c = 5.74$	11.4	4.5	312
$[\text{Co}(\text{en})_2\text{LTCl}]^{2+}\cdot 2\text{Cl}^-$	4.9	Orthorhombic $a = 13.14$ $b = 10.09$ $c = 6.54$	14.8	2.3	621
$[\text{Co}(\text{en})_2\text{LA}_3]^{3+}\cdot 3\text{Cl}^-$	10.0	Orthorhombic $a = 9.82$ $b = 6.41$ $c = 6.12$	13.8	3.5	410
$[\text{Co}(\text{en})_2\text{L}_2\text{T}_2]^{3+}\cdot 3\text{Cl}^-$	3.0	Orthorhombic $a = 12.99$ $b = 9.36$ $c = 6.36$	3.4	2.3	603

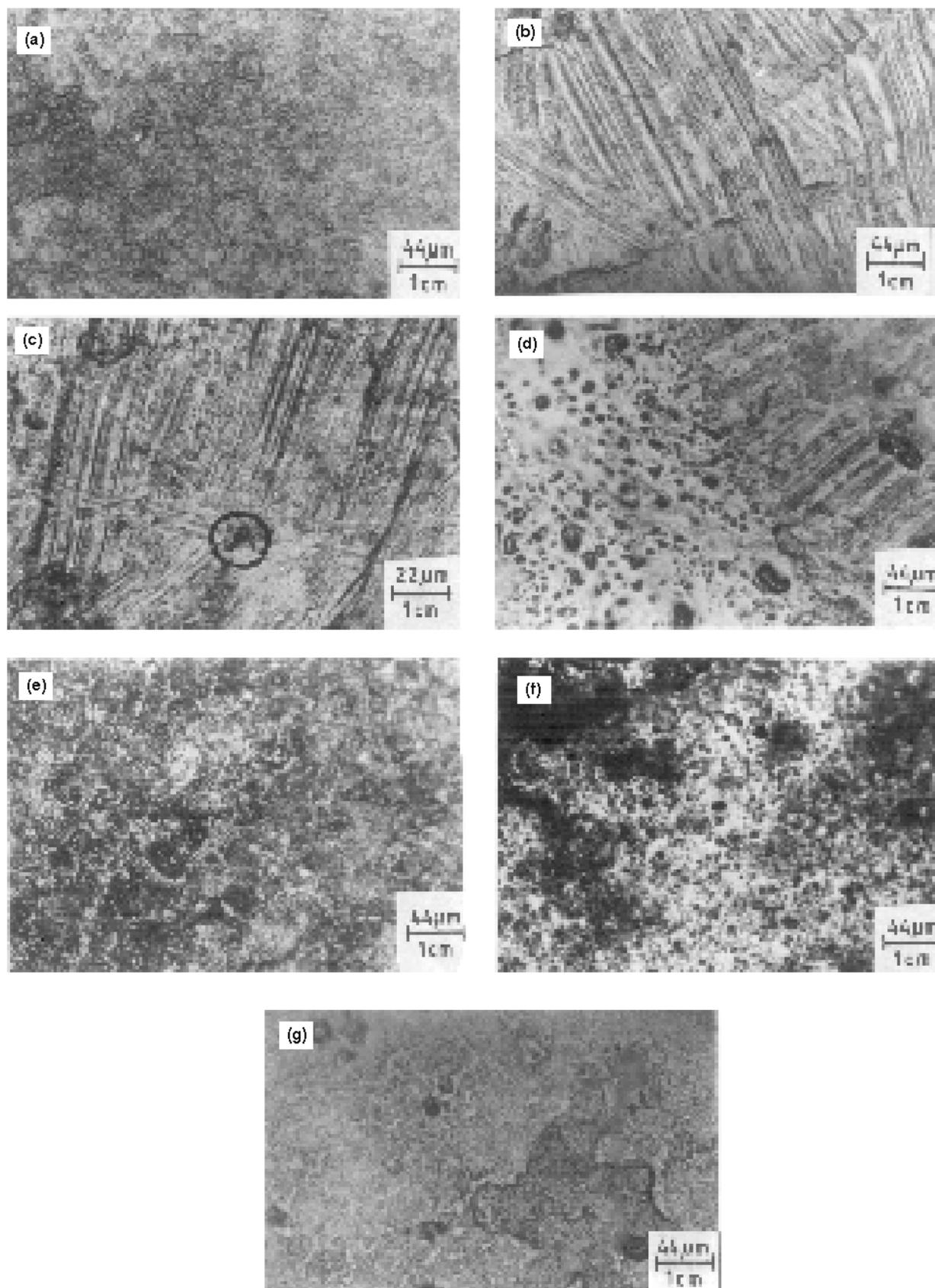


Figure 1. Optical micrograph of the complexes: (a) $[\text{MLCl}]^{2+}$, (b) $[\text{ML}_2]^{3+}$, (c) $[\text{ML}_2]^{3+}$, (d) $[\text{ML}_2]^{3+}$, containing acetone, (e) $[\text{ML}_2\text{T}_2]^{3+}$, (f) $[\text{MLTCI}]^{2+}$ and (g) $[\text{MLA}_3]^{3+}$, $\text{M} = \text{Co}(\text{en})_2$.

4. Conclusions

We have observed that $[\text{Co}(\text{en})_2\text{LCl}]^{2+} \cdot 2\text{Cl}^-$ displays tetragonal structure with coherently scattering domain size of ~ 10 nm. However, $[\text{Co}(\text{en})_2\text{LCl}]^{2+} \cdot 2\text{Cl}^-$ after reaction with the ligand producing $[\text{Co}(\text{en})_2\text{L}_2]^{3+} \cdot 3\text{Cl}^-$ showed orthorhombic structure. The microstructural characterizations of the solidified pellet have shown that $[\text{Co}(\text{en})_2\text{LCl}]^{2+} \cdot 2\text{Cl}^-$ possesses invariably two kinds of contrast, the contrast of the minor phase has been attributed to the formation of $[\text{Co}(\text{en})_2\text{L}_2]^{3+} \cdot 3\text{Cl}^-$ in the system. In contrast to the above, the $[\text{Co}(\text{en})_2\text{L}_2]^{3+} \cdot 3\text{Cl}^-$ complex has given uniform and identical contrast with rod morphology in the form of a bundle which supported the presence of single phase in this case. Further, the treatment of $[\text{Co}(\text{en})_2\text{L}_2]^{3+} \cdot 3\text{Cl}^-$ complex with acetone leads to the transformation of the rod morphology and the changed features matched well with that of $[\text{Co}(\text{en})_2\text{L}_2\text{T}_2]^{3+} \cdot 3\text{Cl}^-$ micrograph which has been explained on the basis of the similarity between the functional groups ($> \text{C}=\text{O}$) in both acetone and thymine.

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