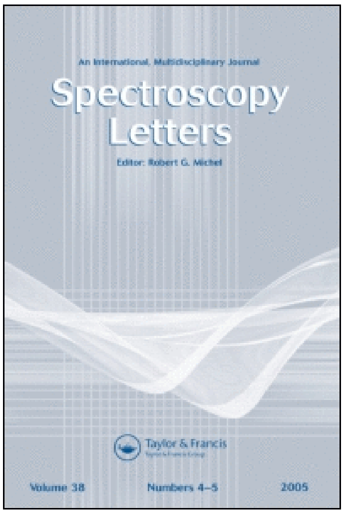

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STUDY OF INFRARED AND ELECTRONIC SPECTRA OF N-EXADECYL-8-HYDROXY-2-QUINOLINECARBOXAMIDE COMPLEXES

Key Words: Infrared spectra; electronic spectra; amphiphilic complexes; monolayer

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ABSTRACT

The infrared and electronic spectra of twelve amphiphilic complexes of N-hexadecyl-8-hydroxy-2-quinoline carboxamide (HL) have been investigated. In IR spectra a linear relationship between the ν (C-O) frequency in C-O-M bond of the complexes and the relative atomic weight of the central metal ions and a linear relationship between the ν (C-O) frequency and the ionization potential of the central metal ($M \rightarrow M^{2+}(g)+2e$) were obtained. These complexes appeared to fall into two groups. One is the complexes of closed-shell metal ions such as Ca(II), Mg(II), Zn(II), Cd(II), Al(III), La(III) and Gd(III) ion, the other is the complexes of transitional metal ions such as Mn(II), Co(II), Ni(II) and Cu(II) ion. All these complexes can form stable monolayer and can be deposited as uniform LB films.

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INTRODUCTION

Recently, Tang et al.[1,2] found that 8-hydroxyquinoline aluminum (Alq_3) can be used as emitting elements in electroluminescent (EL) devices. In the EL diode they designed, high external quantum efficiency and brightness are achievable at a driving voltage below 10 V. After Tang's research works, other 8-hydroxy quinoline derivatives-metal complexes, such as Znq_2, Beq_2, Mgq_2, $Zn(mq)_2$, $Be(mq)_2$, $Al(prq)_2$ (mq and prq are 2-methyl-8-hydroxyquinoline and 7-propyl-8-hydroxyquinoline, respectively) were also used as emitters.[3] Since LB films technique make it possible to prepare organic functional ultrathin films with a controlled thickness at a molecular size and with defined molecular orientation,[4-6] therefore, if some new amphiphilic complexes with 8-hydroxyquinoline can be synthesized and further be incorporated in LB films, these films may be used as the emitting layer of EL devices. These emitting layer can be fabricated more conveniently than the general vacuum deposited technique. Actually, the LB films of the amphiphilic complexes, bis[N-hexadecyl-8-hydroxy-2-quinoline carboxamide] lanthanum [$LaL_2(H_2O)_4Cl$] and bis[N-hexadecyl-8-hydroxy-2-quinoline carboxamide]cadmium [CdL_2], have been used as emitting layer in electroluminescent (EL) devices.[7-9] Green-yellow emission (the EL peak wavelengths were 515 and 490 nm, respectively) with a luminance of about 330 and 1200 cd/m^2, respectively, were achieved. In the present work, the infrared and electronic spectra of ten new amphiphilic complexes of N-hexadecyl-8-hydroxy-2-quinolinecarboxamide (HL) and $LaL_2(H_2O)_4Cl$ and CdL_2 have been investigated, their monolayer-forming ability was discussed.

EXPERIMENTAL

Reagents

The amphiphilic ligand, N-hexadecyl-8-hydroxy-2-quinolinecarboxamide (HL, the structure was shown in the inset in Fig.5) and its complexes were prepared by the method described earlier.[10-11] All other chemicals were of A.R. grade, purchased from Shanghai Chemical Reagents Co. Solvents were purified by standard procedures.

Measurements

IR spectra were recorded as KBr pellets, by a Nicolet Model 170 SX FTIR spectrometer. Electronic spectra were determined with a Shimadzu Model 3100 UV-VIS-NIR recording spectrophotometer.

RESULTS AND DISCUSSION

Infrared Spectra

The relevant infrared absorption bands of the ligand and its complexes with their possible assignment are given in Table 1, only the most characteristic bands were given. Some major bands (Fig.1) at *ca.* 1600, 1500, 1360, 1311, 1040, 850 and 756 cm $^{-1}$ for the complexes are assigned to be the absorption of quinoline ring and aromatic CH bonds[4,10] and not be shown. An intense broad band at 3306 cm $^{-1}$ and a band at 1220 cm $^{-1}$ in the spectra of HL are the characteristics of OH groups. These bands are absent from the spectra of the complexes, indicating the deprotonation of HL and coordination through the oxygen atom. The disappearance of the band at 650 cm $^{-1}$, due to the out-of plane blending of OH, also supports this observation. But for the spectra of complexes AlL_2OH and $ML_2(H_2O)_4Cl$ (M=La(III), Gd(III)), the broad bands at 3306 cm $^{-1}$ shifted to 3390-3460 cm $^{-1}$. It is the results of OH group or water molecules, which were confirmed by elemental analyses and thermoanalyses.[12] Strong evidence for water coordination in the complexes $ML_2(H_2O)_4Cl$ is the appearance of a broad band at *ca.* 892 cm $^{-1}$ due to the rocking vibration of H_2O.[13,14]

Comparing the IR spectra of the complexes with that of the ligand, the ν (C-O) frequency (1650 cm $^{-1}$) in the ligand is shifted down to *ca.* 1622 cm $^{-1}$ in the complexes (except for MgL_2, CaL_2 and AlL_2OH), indicating the C=O may be coordinated with these metal ions through oxygen atom. The fact that C=O was not coordinated with Mg(II), Ca(II) and Al(III) was due to the atomic orbitals of these three metal ions are blended together to give a sp^3 hybrid orbital and only four coordination is presented.

These complexes show strong and sharp bands in the range 1430-1458 cm $^{-1}$, which are assigned to ν (C=N), the frequencies of these bands are lowered by *ca.* 4~32 cm $^{-1}$ comparing with that in HL, indicating the participation of the heterocyclic nitrogen atom in bonding.

In the low frequency region, the band observed in the region of 450-501 cm $^{-1}$ attributed to ν (M-O) in the complexes.[15-18] The order of ν (M-O) frequencies for divalent metal ion complexes is nearly in agreement with that of the ionic potential, Z/r (Z and r are the charge and radius of metal ion respectively) of corresponding central metal ions. The radius order of the metal ions is as follow:

Pb(0.120) < Ca(0.099) < Cd(0.097) < Mn(0.080) < Co(0.074), Zn(0.074) < Ni(0.072) < Cu(0.069) < Mg(0.065 nm)

TABLE 1. IR Absorption Frequencies of HL and Its Complexes (cm^{-1})

Compound	ν OH	ν CH	ν CH	ν C=O	ν C=N	ν (C-O)	δ (CH)	ν (C-O)
HL	3306	2925	2856	1650	1462	1096	723	
MnL_2		2926	2854	1623	1447	1107	722	481
CoL_2		2924	2852	1622	1442	1114	723	482
NiL_2		2931	2860	1623	1448	1117	723	501
CuLCl		2924	2861	1631	1441	1124	723	498
ZnL_2		2924	2855	1632	1444	1117	721	500
CdL_2		2924	2854	1624	1441	1116	720	472
PbL_2		2924	2854	1631	1441	1103	723	450
$LaL_2(H_2O)_4Cl$	3416	2927	2853	1622	1458	1108	722	464 484
$GdL_2(H_2O)_4Cl$	3460	2924	2854	1631	1455	1110	721	465 490
MgL_2		2925	2852	1653	1447	1124	722	490
CaL_2		2925	2852	1653	1430	1123	722	470
AlL_2OH	3390	2925	2852	1653	1442	1124	721	470

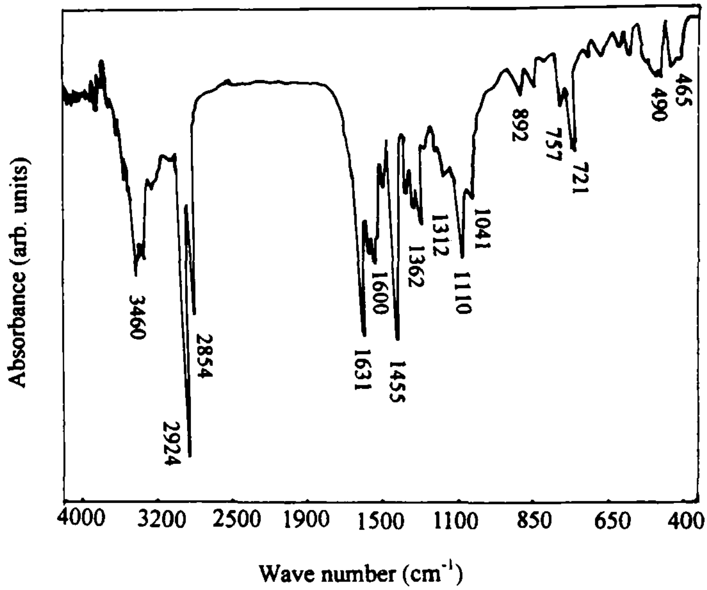

FIG. 1 IR spectrum of amphiphilic complex $GaL_2(H_2O)_2Cl$.

the ν (M-O) frequencies of the corresponding complexes are 450, 470, 472, 481, 482, 500, 501, 498 and 490 cm^{-1}, respectively.

All these changes in frequencies suggest that the metal ions in complexes (except for Mg(II), Ca(II) and Al(III)) are bonded to the ligand through the heterocyclic nitrogen, the phenolic oxygen and the carbonyl oxygen, that is, a tridentate coordination mode of HL to metal ions is formed. Further confirmation regarding the coordination mode of HL and the geometry of all these complexes has been obtained from electronic spectra, magnetic susceptibility measurement and TGA-DTA studies.[12]

In the IR spectra of all the complexes studied, a strong peak appears at about 1120 cm^{-1}, which is the characteristic of the C-O vibration in C-O-M bond of the complexes. Comparing the position of this peak in the ligand (1096 cm^{-1}), the considerable shift of this peak again suggests the participation of phenolic oxygen atom of HL in bonding. The exact position of the ν (C-O) vibration for the complexes was found to vary depending on the metal complex. Plotting the position of this peak against the relative atomic weight of the metal, the points appear to fall into two groups (Fig.2). The points for the Mg(II), Ca(II), Zn(II), Cd(II), Pb(II), Al(III), La(III) and Gd(III) complexes (A group) obey a relationship similar to that found for the metal carbonates.[19] On the other hand, the points for the transition-metal complexes such as Mn(II), Co(II), Ni(II) and Cu(II) complexes (B group) fall another straight line of quite different slope, the absorption frequency in this case increasing sharply with the increasing relative atomic weight of the metal. The magnitudes of the shifts of ν (C-O) follow the well-known Irving-Williams order:

Mn (11cm^{-1}) < Co (18cm^{-1}) < Ni(21cm^{-1}) < Cu(28cm^{-1}) > Zn (21cm^{-1})

The difference just noted suggests that a fundamental difference in structure of some sort may exist between the two groups of complexes.

C.L.Van [20] considered this difference was that only M-O bonding is formed in the complexes of A-group metal ions, and both M-O and M-N bonding are formed in those of B-group metal ions. P.G.Charles[21] considered that this difference may be the possible participation of 3d orbitals in B-group metal-ligand bonding or the difference in crystal structure for the two groups of complexes. But magnetic susceptibility measurements indicated no participation of 3d orbitals in all metal-ligand bonding and L.L.Merrit [22] inferred $Mq_2(H_2O)_2$ (q=8-quinoline, M=Mn, Co, Ni, Zn, Cd, Pb) had the same crystal structures. We considered this difference was caused by the difference of the strength of M-O and M-N bonding in different complexes. In the complexes of A-group metal ions, the metal ions react primarily with the negatively charged oxygen, the M-O bonding play more important role than M-N bonding. On the contrary, B-group metal ions react primarily with the covalent nitrogen, the M-N bonding is stronger than M-O bonding. That is, the M-N bonding play more important role in the complexes of B-group metal ions. These results are in agreement with Pearson's solf-hard acid-base theory. The most strong bonds result from hard-hard acid-base and solf-solf acid-base combination. Since the phenolic O atom and heterocyclic N atom of HL are hard and middle-hard bases, respectively, and A-group metal ions are hard acid and B-group metal ions are middle-hard bases, therefore, the M-O bonding in A-group is stronger than that in B-group complexes and the M-N bonding in B-group is stronger than that in A-group complexes.

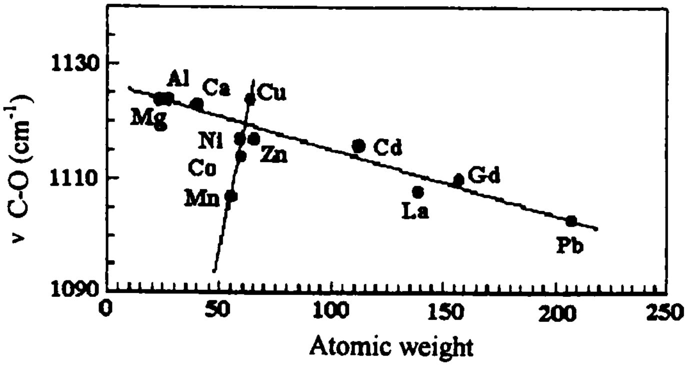

FIG.2 The dependence of ν (C-O) frequency on the atomic weight of the metal in HL complexes.

Some authors[20,23,24] have already pointed out that there is a linear relation between the ionization potential for a series of metals and the stability of the corresponding complexes formed by their ions with a given ligand in an aqueous medium. It is interesting that there is a linear relation between the ν (C-O) frequency of the divalent metal-HL complexes and the ionization potential (I) of the corresponding complexes:

$$\nu\,(C\text{-}O) = p\,(I - q)$$

where I is the ionization potential in eV, i.e. the energy of the reaction: M→ M^{2+} +2 electrons, in the gas phase; p and q are constants only depending on the ligand and temperature. The relation has been represented in Fig.3. These points also fall into two groups of different p and q values. For A-group complexes, p = -1.85 $cm^{-1}\cdot eV^{-1}$, q = 630 eV^{-1}; for B-group complexes, p = 3.78 $cm^{-1}\cdot eV^{-1}$, q = -270 eV^{-1}. Comparing Fig.3 with Fig.2, only Pb complex is exception. Pb shifts from A-group in Fig.2 to B-group in Fig.3. Actually, although Pb has a closed-shell electronic structure ($5d^{10}6s^2$), but Pb has a big radius and a large polarization. When Pb coordinates with N, O atoms, quite a covalent character exists in Pb-N and Pb-O bonds.

Electronic Spectra

The electronic spectral data of the complexes in DMF are set out in Table 2. The features representative of A-group ($GdL_2(H_2O)_4Cl$) and B-group complexes

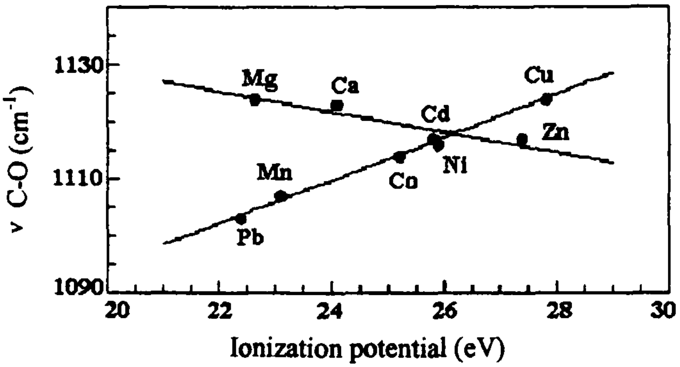

FIG.3 The dependence of v (C-O) frequency on the ionization potential of the metal (M → M^{2+}(g)+2e) in HL complexes.

TABLE 2. Electronic Spectra Data of the Ligand and Its Complexes (in DMF, 1.0 × 10^{-4} mol/L)

compound	charge transfer bands			ligand field bands
	^1B_b	^1L_b	^1L_a	
HL	262	309	352	
MnL_2	268	307(sh)	348	428
CoL_2	275		353	502
NiL_2	264	283	356	461
CuLCl	276	310(sh)	357	450
ZnL_2		282.5	350	446
CdL_2	264	284(sh)	349 352	450
PbL_2	266	282	355	455
$LaL_2(H_2O)_4Cl$	265	311(sh)	347 352	405
$GdL_2(H_2O)_4Cl$	266		344 352	427
MgL_2	264		347 352	445
CaL_2	265	312(sh)	347 352	410
AlL_2OH	265		348 352	420

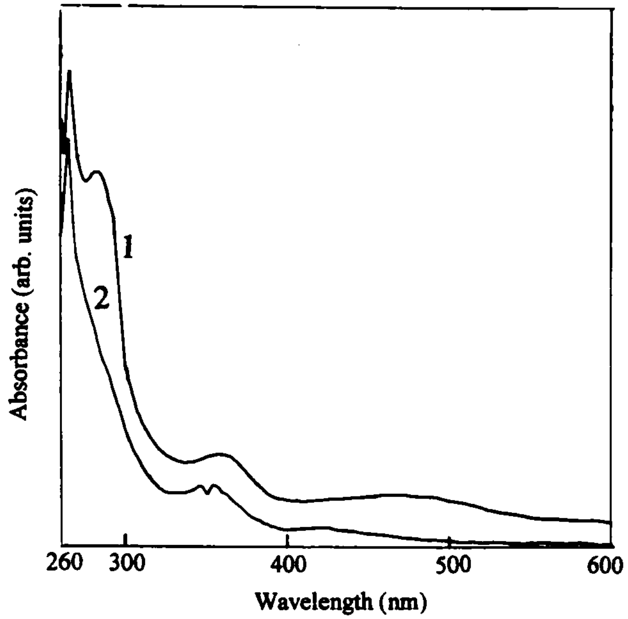

FIG.4 Electronic spectra of amphiphilic complexes. 1, NiL_2; 2, $GdL_2(H_2O)_4Cl$.

(NiL_2) are shown in Fig.4. Two strong bands near 265 and 350 nm, one shoulder at 284~310 nm and one band in the region of 410-502 nm are assigned to the ^1B_b, ^1L_b, ^1L_a band of quinoline ring[25] and the LMCT (ligand to metal charge transfer) band, respectively. Apparently the electronic spectra of the complexes of both A-group and B-group metal ions have the similar characteristics, respectively, suggesting each-group metal ions have similar effects on the vibrations responsible for the absorption peaks. The greatest difference between A-group and B-group complexes was ^1L_a band and the ligand field bands. The ^1L_a band was split into two bands in A-group complexes at *ca.* 347 and 352 nm. Since ^1L_a band is ascribed to the charge-transfer from the phenol ring to the heterocyclic,[26] therefore, the more ^1L_a band bathochromically shifts, the stronger the M-N bonding in the complexes; and the more ^1L_a band hypsochromically shifts, the stronger the M-O bonding. It can be seen from Table 2 that the ^1L_a band of the

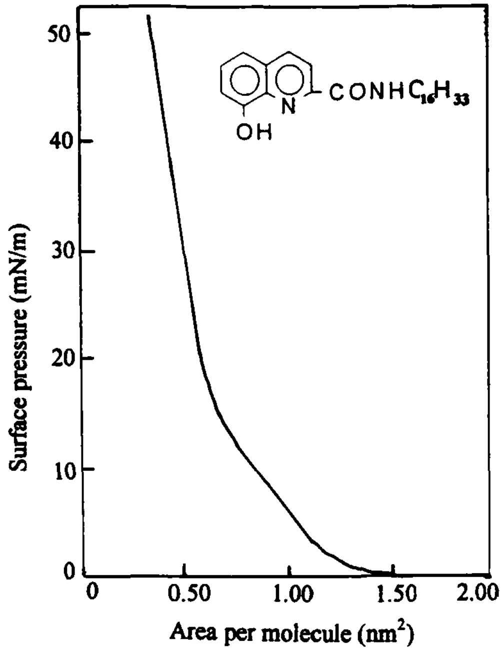

FIG.5 The π -A isotherms of $GdL_2(H_2O)_4Cl$ at an air/water interface. The inset is the molecular structure of N-hexadecyl-8-hydroxy-2-quinoline carboxamide.

complexes of Co(II), Ni(II), Cu(II) and Pb(II) have bathochromically shifted *ca.* 1-5 nm, it indicates that the M-N bonding in these complexes is stronger than the M-O bonding. On the contrary, the ^1L_a band of the complexes of Zn(II), Ca(II), Mg(II), Cd(II), La(III), Gd(III) and Al(III) have hypsochromically shifted *ca.* 2-8 nm, it indicates that the M-O bonding in these complexes is stronger than the M-N bonding. These results were in accord with that obtained from the infrared spectra studies above.

The Formation of Langmuir-Blodgett(LB) Films of HL Complexes

HL complex was spread onto pure water subphase from chloroform. Generally 30 min was allowed for chloroform evaporation. The monolayer was then compressed by two movable Teflon barries at a rate of *ca.* 0.03 $nm^2 \cdot molecule^{-1} \cdot min^{-1}$, and a surface pressure (π) *vs.* area per molecule (A) isotherm was recorded with a WM-1 Langmuir trough system, which is a fully computerized and programmable apparatus.

Fig.5 shows a typical surface pressure-area (π -A) isotherm of complex $GdL_2(H_2O)_4Cl$ with a high collapse surface pressure of *ca.* 52 mN/m, indicating that $GdL_2(H_2O)_4Cl$ can form stable and dense monolayer at the air-water interface.

The average area per $GdL_2(H_2O)_4Cl$ molecule, obtained by extrapolating the π -A isotherm to zero surface pressure, is 0.73 nm^2. This monolayer can easily be transferred onto quartz glass at a surface pressure of 25 mN/m. The monolayer deposition is reproducible and the obtained LB films have vertical homogeneity. The π -A isotherms and the LB films of the other complexes show similar character. Since these complexes have stronger fluorescence, we hope they, especially AlL_2OH and ZnL_2, could be used in architecture of electroluminescent devices. A more thorough investigation are in progress.

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REFERENCES

1. C.W.Tang and S.A.VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913.
2. C.W.Tang, S.A.VanSlyke, and C.H.Chen, *J. Appl. Phys.*, 1989, **65**, 3610.
3. Y.Hamada, T.Sano, M.Fujita, T.Fujii, Y.Nishio, and K.Shibata, *Jpn. J. Appl. Phys.*, 1993, 32, L514.
4. J.-M. Ouyang, Z.-H. Tai, and W.-X. Tang, *J. Mater. Chem.*, 1996, **6**(6), 963.
5. F.L.Carter, *Molecular Electronic Devices I*, Dekker, New York, 1982.
6. M.Schmelzer, S.Roth, and C.P.Niesert, *Thin Solid Films*, 1993, **235**, 210.
7. J.-M. Ouyang, L. Li, Z.-H. Tai, Z.-H. Lu, G-M Wang, *J. Chem. Soc., Chem. Commun.*, 1997, 815.
8. J.-M. Ouyang, L. Li, Z.-H. Tai, Z.-H. Lu, G.-M. Wang, *Chem. Lett.*, 1997, 815.
9. J.-M. Ouyang, C.-Y. Jiang, Z.-H. Tai, W.-X. Tang, *Jinan Daxue Xuebao*, 1997, **18**(5), 51

10. J.-M. Ouyang, Z.-H. Tai, C.-Y. Jiang, W.-X. Tang, *Spectroscopy Letters*, 1996, **29**(5), 763.

11. J.-M. Ouyang, Z.-H. Tai, C.-Y. Jiang, W.-X. Tang, *Wuji Huaxue Xuebao*, 1997, **13**(3), 315

12. The physical properties of the complexes in details will be described elsewhere.

13. H.M.Chawla, U.Hooda and V.Singh, *Synth. Teact. Inorg. Met.-Org. Chem.*, 1996, **26**, 775.

14. G.C.Percy. *J. Inorg. Nucl. Chem.*, 1975, **37**, 2071.

15. K.Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 4th Ed. John Willy and Sons, New York, 1963.

16. F.A.Cotton, *Advanced Inorganic Chemistry*, 5th Ed. Wiley, New York, 1988.

17. B.V.Patel and B.T.Thather, *Synth. React. Inorg. Met.-Org. Chem.*, 1986, **16**, 1319.

18. W.T.Grody, *J. Chem. Phys.*, 1946, **14**, 305.

19. J.M.Hunt, *Anal. Chem.*, 1950, **22**, 1478.

20. C.L.Van Panthaleon Van Eck, *Rec. Trav. Chim.*, 1953, **72**, 50.

21. P.G.Charles, H.Freiser and R.Friedel, *Spectrochim. Acta*, 1956, **8**, 1.

22. L.L.Merrit, *Anal. Chem.*, 1953, **25**, 718.

23. L.H.Ahrens, *Nature*, 1952, **169**, 163.

24. W.S.Fyte, *J. Chem. Soc.*, 1952,2018.

25. H.H.Perkampus and K.Kortum, *Z. Analty. Chem.*, 1962, **190**, 111.

26. L.Morpurgo and J.P.Williams, *J. Chem. Soc.*, 1966, 73.

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