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SPECTRAL AND THERMAL STUDIES ON COPPER(II) COMPLEXES OF ACENAPHTHAQUINONEMONO-(4-METHYLQUINOLINYL)HYDRAZONE

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Cu(II) complexes of acenaphthaquinonemono(4-methylquinolinyl)hydrazone (AMH) of general composition [$CuLX_2$] (where *L* =AMH; *X* =Cl, Br, I, OAc or NO_3) with the exception of sulphato complex, where the composition is found to be [$CuLSO_4$]$_2$ have been synthesized and characterized by elemental analyses, magnetic moment measurements, conductivity measurements, IR, electronic and EPR spectral techniques and by thermal analysis. A planar geometry is indicated for all the complexes. TG curves show one step decomposition of complexes and formation of Cu_2O at the end of the step.

Keywords: complexes, coordination chemistry

Introduction

Coordination chemistry of substituted hydrazones has been provided by remarkable anticancer [1], antibacterial [1], antileukemic [2] activity observed for these compounds which has since been shown to be related to their metal complexing ability. Substituted hydrazones exhibit a wide range of stereochemistries on complexation with metal ions [3–5]. In this paper we describe the synthesis, spectroscopic characterization and thermal studies on Cu(II) complexes of AMH.

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Experimental

Physical measurements

The complexes were analysed for C, H and N in Microanalytical Laboratory, I.I.T., New Delhi (India). Copper was estimated on a Perkin-Elmer 703 atomic absorption spectrophotometer in solutions prepared by decomposing the complexes in conc. HNO_3. Magnetic susceptibility measurements at room temperature were carried out in the powdered state on a vibrating sample magnetometer PAR 155 with 5000G field strength, using high purity nickel metal (saturation moment 55 emu g^{-1}) as calibrant. Molar conductances of complexes in DMF solution were measured at room temperature on a systronic digital direct reading conductivity meter model 304 using platinum electrodes. The electronic spectra (900–300 nm) of the complexes in ethanol were recorded on a Perkin-Elmer 554 UV visible spectrometer. IR spectra were reported in the range 4000–400 and 800–200 cm^{-1} as KBr and CsI discs, respectively. EPR spectra in polycrystalline state at room temperature were recorded on a varian model E-4 spectrometer (X-band) using DPPH ($g = 2.0036$) as the standard. The PMR spectra of the ligand was recorded in $CDCl_3$ on Perkin-Elmer model R-32 NMR spectrometer operated at 90 MHz. TG was recorded on Stanton Red-Croft TG 770 thermobalance using 5–10 mg samples and the heating rate was 3 $deg \cdot min^{-1}$.

Materials and methods

All the reagents used were of commercial grade and were used without further purification.

Preparation of AMH

2-Chloro-4-methylquinoline synthesized by reported method [6–7] was refluxed with hydrazinehydrate which gives 2-hydrazino-4-methylquinoline. 2-Hydrazino-4-methylquinoline (3.46 g, 0.02 mol) was dissolved in 25 mlof HCl. Acenapththaquinone (3.64 g, 0.02 mol) dissolved in 100 ml of ethanol was added to 4-methylquinolinylhydrazinehydrochloride. The contents were refluxed for half an hour and the product obtained was filtered, recrystallized from ethanol and dried in vacuum desiccator over P_2O_5 (Found: C, 78.68; H, 4.51; N, 12.43%. Calc. for $C_{12}H_{15}N_3O$: C, 78.33; H, 4.45; N, 12.46%).

The purity of the ligand was checked by TLC and characterized by elemental analysis, IR and PMR spectroscopy (δ value ppm) in $CDCl_3$ [2.4(s, 3H, $-C-CH_3$); 7.2–7.9(m, 9H, aromatic protons); 8.8(s, 1H, N-NH-C); 8.2(s, 1H, ring NH protons)].

Synthesis of complexes

Ethanolic-water solution of various Cu(II) salts (1 mmol) was added to an ethanolic solution of AMH (2 mmol). The resulting mixture was refluxed for 3h and the volume was then reduced to one-third by distillation under reduced pressure. On cooling shining crystals of complexes were separated out. These were filtered and washed with water and benzene and purity was checked by TLC. Other ratio of M:L were also tried, but in every case, complexes with similar compositions were observed.

Results and discussion

AMH reacts with Cu(II) salts in neutral condition and produces $[CuLX_2]$ (where L = AMH and X = Cl, Br, I, OAc, or NO_3) with the exception of sulphato complex where the composition is found to be $[MLSO_4]_2$ (Table 1). These complexes are insoluble in water and common organic solvents but have appreciable solubility in DMF and ethanol. The molar conductivity of the complexes have been found to be consistent with non-electrolytic nature [8].

Magnetic measurements

The room temperature magnetic moments (Table 1) of the complexes fall mainly in the range 1.7–1.9 B.M. very close to the spin-only value of 1.73 B.M. for a d^9 ion and are consistent with planar coordination around copper.

IR spectra

The significant IR bands are presented in Table 2. The IR spectrum of AMH shows an intense strong band at 1670 cm^{-1} due to $\nu_{C=O}$, undergoes a negative shift of 20–40 cm^{-1}; pointing to the oxygen atom of the >C=O group as a possible coordination site in the complexes. The other strong band appearing at 1605 cm^{-1} due to $\nu_{C=N}$ in the free AMH spectrum undergoes a negative shift of ~ 10 cm^{-1} in the complexes indicates the involvement of the nitrogen of C=N group in bonding. However the band due to ν_{NH} at 3400 cm^{-1} in AMH remains intact in the complexes indicating non-involvement of the nitrogen of –NH of hydrazino group. The low frequency bands in the regions 460–445 and 410–380 cm^{-1} in the complexes are attributed to ν_{Cu-O} and ν_{Cu-N} respectively [9–11]. The other low frequency bands in the regions 340–330 and 250– 240 cm^{-1} in the complexes are assigned to ν_{Cu-Cl} and ν_{Cu-Br} respectively indicating that chlorine and bromine is terminally bonded [12–13] rather than bridging. The ratio ν_{Cu-Br}/ν_{Cu-Cl} is 0.69 in all the cases which are consistent with the values for the complexes of first row transition metals [14].

Absorption bands corresponding to metal-iodide strengths could not be assigned as they were beyond the range of instrument. The additional bands observed in the complexes having polyatomic ions, confirm the monodentate nature of acetato [15] and nitrato [16, 17] groups. The band at ~ 320 and 300 cm^{-1} are

Table 1 Analytical and magnetic moment data for complexes

Complex	Analysis: Found (Calc.) %				Colour	μ_{eff} /
	C	H	N	Cu		B.M.
[$CuLCl_2$]	55.61 (55.99)	3.00 (3.18)	8.72 (8.90)	13.30 (13.47)	Dark brown	1.90
[$CuLBr_2$]	46.92 (47.11)	2.71 (2.67)	4.23 (4.79)	11.00 (11.33)	Dark brown	1.79
[$CuLI_2$]	40.46 (40.30)	2.41 (2.29)	6.11 (6.41)	9.52 (9.71)	Dark brown	1.80
[$CuL(OAc)_2$]	60.18 (60.16)	3.26 (3.04)	7.90 (8.09)	12.00 (12.25)	Dark brown	1.89
[$CuL(NO_3)_2$]	50.02 (50.32)	2.61 (2.85)	13.00 (13.34)	11.91 (12.11)	Dark brown	1.76
[$CuLSO_4$]$_2$	53.01 (53.16)	7.92 (8.02)	8.10 (8.45)	12.44 (12.79)	Black	1.76

Table 2 Some characteristic IR bands (cm^{-1}) and molar conductance of the complexes

Compound	$\nu_{C=O}$	$\nu_{C=N}$	$\nu_{Cu\text{-}N}$	$\nu_{Cu\text{-}O}$	$\nu_{Cu\text{-}X}$	Molar conductance/ $cm^2\ \Lambda\ mol^{-1}$
[AMH (L)]	1670	1605	–	–	–	11.54
[$CuLCl_2$]	1655	1595	400	450	340	29.88
[$CuLBr_2$]	1640	1590	410	450	240	38.83
[$CuLI_2$]	1645	1590	385	435	–	44.19
[$CuL(OAc)_2$]	1650	1595	380	450	320	29.37
[$CuL(NO_3)_2$]	1645	1590	390	445	300	36.67
[$CuLSO_4$]$_2$	1660	1595	385	445	950 (ν_1), 1050, 1100, 1170 (ν_3), 610 (ν_4)	46.12

assigned to ν_{Cu-OAc} and ν_{Cu-NO_3} respectively. In sulphato complexes, ν_1 band is a weak band while ν_4 is of medium intensity. The strong band ν_3 is found to split into three bands in the range 1170–1100 cm^{-1} indicated that SO_4^{2-} ion acts as a bridging bidentate ligand [18–21] and the complex so formed is dimeric in nature.

Electronic spectra

The significant electronic absorption bands in the spectra of the complexes in ethanol presented in Table 3. The electronic spectra of the complexes display two weak and broad ligand transitions in the vicinity of 20700–19000 cm^{-1} and 15800–15400 cm^{-1} in an idealised square planar symmetry. The two bands may be assigned as $2\,B_{1g} \rightarrow 2\,E_g$ and $2\,B_{1g} \rightarrow 2\,A_{1g}$ transitions respectively as suggested by Figgis [22] and Dave *et al.* [23]. These bands are comparable in positions with the earlier reported square planar copper(II) complexes which leads to believe that all the Cu(II) complexes are essentially planar. One or two bands are also observed in most of the complexes in the region 32000–23000 cm^{-1} are reasonably taken as Ligand → Metal charge transfer bands as suggested by other workers [24–26].

Table 3 Electronic spectral data (cm^{-1}) of copper(II) complexes

Complex	$2\,B_{1g} \rightarrow 2\,A_{1g}$	$2\,B_{1g} \rightarrow 2\,E_g$	Charge transfer
$[CuLCl_2]$	15800	20080	23470, 28900
$[CuLBr_2]$	15680	20700	—
$[CuLI_2]$	15620	20400	—
$[CuL(OAc)_2]$	15800	20270	30300
$[CuL(NO_3)_2]$	15800	20600	25000, 31250
$[CuLSO_4]_2$	15800	20080	22730

EPR spectra

EPR spectral data of few complexes were recorded in polycrystalline state at room temperature (Table 4). The spectra of the complexes show a strong signal at high field and a weak one at low field corresponding to $g_\perp$ and $g_\parallel$ respectively. For tetrahedral complexes g_{av} is found to be isotropic. The anisotropy due to Jahn-Teller distortion is beyond detection at room temperature. The $g_\perp$, $g_\parallel$ and g_{av} calculated for the isolated complexes are in consistent with square-planar geometry [27–28] and $g_\parallel$ values for the present complex show considerable covalent character. The EPR spectra at liquid N_2 could not provide any additional information.

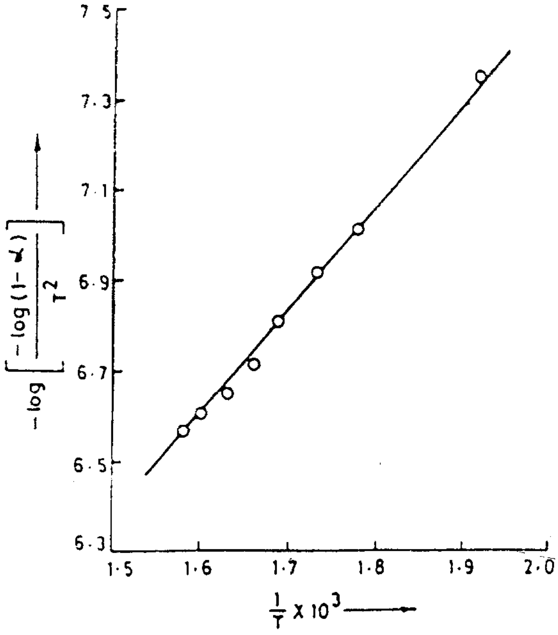

Fig. 1a Kinetic parameters from TG $CuLCl_2$

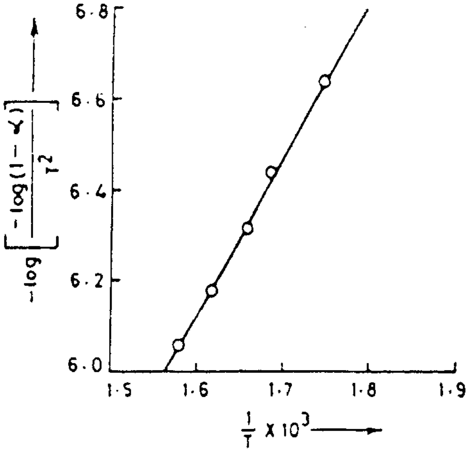

Fig. 1b Kinetic parameters from TG $CuLBr_2$,

Thermal studies

Thermal studies have been carried out to evaluate kinetic parameters [29–32] of solid state reactions involving weight loss (or gain). Freeman and Carroll [30] have stated some of the advantages of this method over conventional isothermal studies. From TG curves, the order of reaction (*n*) and activation energy (*E*) of the reactions have been enumerated. The weight change is plotted on the ordinate

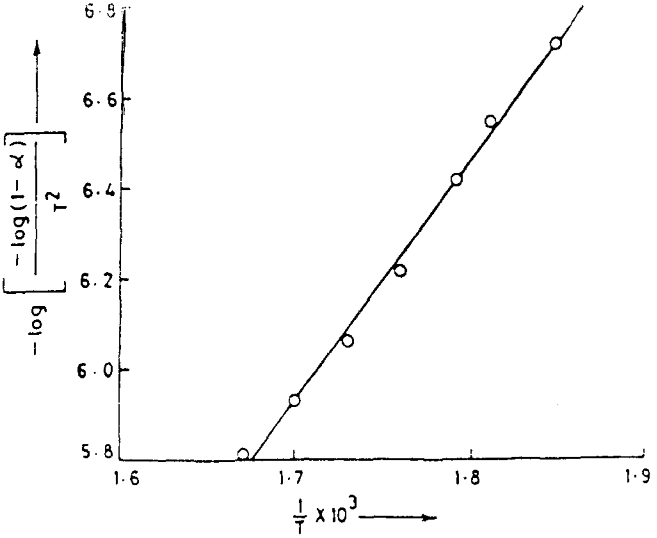

Fig. 1c Kinetic parameters from TG $CuLI_2$

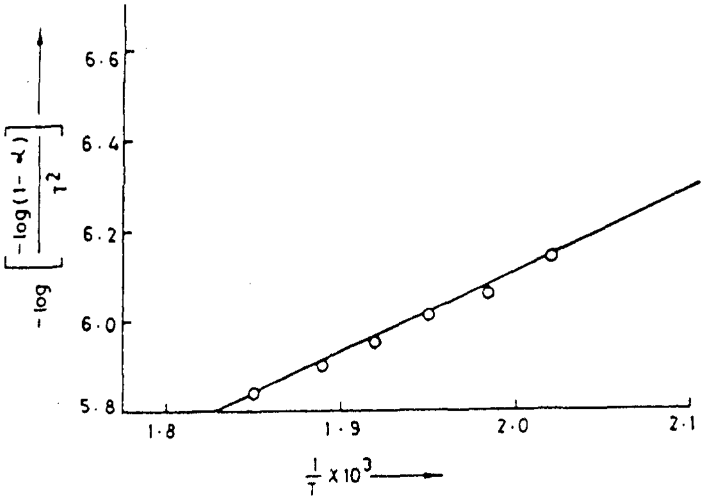

Fig. 1d Kinetic parameters from TG $CuL(OAc)_2$

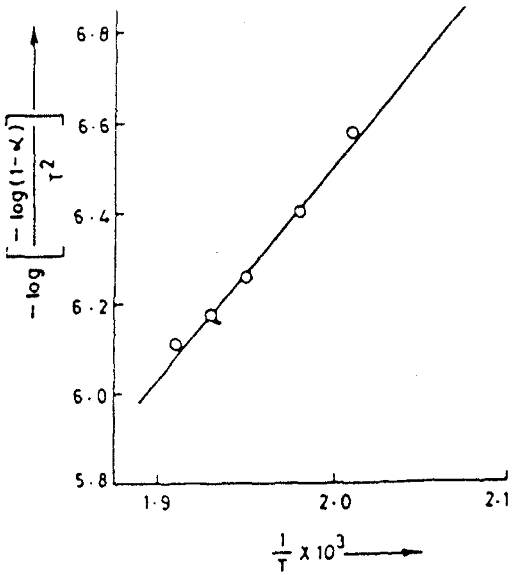

Fig. 1e Kinetic parameters from TG CuL(NO3)2

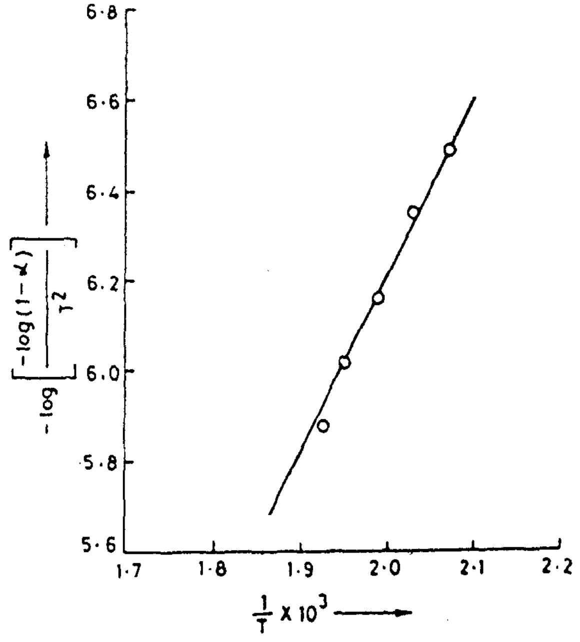

Fig. 1f Kinetic parameters from TG [CuLSO4]2

Table 4 Room temperature EPR spectral parameters of copper(II) complexes in polycrystalline state

Complex	$g_{\parallel}$	$g_{\perp}$	g_{av}	g_{iso}
[$CuLCl_2$]	2.139	2.069	2.092	—
[$CuLBr_2$]	2.157	2.069	2.096	—
[$CuL(OAc)_2$]	—	—	—	2.076
[$CuL(NO_3)_2$]	2.138	2.028	2.065	—

with decreasing weight downwards and temperature (*T*) on the abscissa increasing from left to right. The methods of Coats and Redfern [33] has been used for deriving kinetic parameters.

The complexes [$CuLCl_2$], [$CuLBr_2$], [$CuLI_2$], [$CuL(OAc)_2$], [$CuL(NO_3)_2$], [$CuLSO_4$]$_2$ are stable upto 393, 423, 513, 483, 473 and 473 K respectively. The decomposition of these complexes continues upto 1202, 1033, 953, 1193, 1183, 823 K respectively. In all the cases, a horizontal plateau in TG curve is observed indicating one step decomposition as shown by the presence of breaks in TG curves. The weight loss of 82.92% (Calc. 84.72) for [$CuLCl_2$], 84.31% (Calc. 85.74) for [$CuLBr_2$], 82.04% (Calc. 81.68) for [$CuLI_2$], 79.89% (Calc. 79.11) for [$CuL(OAc)_2$], 76.19% (Calc. 76.00) for [$CuL(NO_3)_2$] and 84.00% (Calc. 84.91) for [$CuLSO_4$]$_2$ corresponds to the formation of Cu_2O.

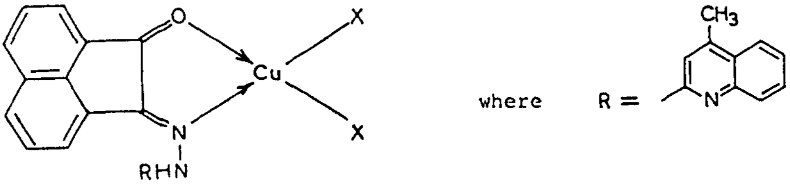

Fig. 2 [$CuLX_2$] (where *L* = AMH; *X* = Cl^-, Br^-, I^- OAc^-, NO_3^-)

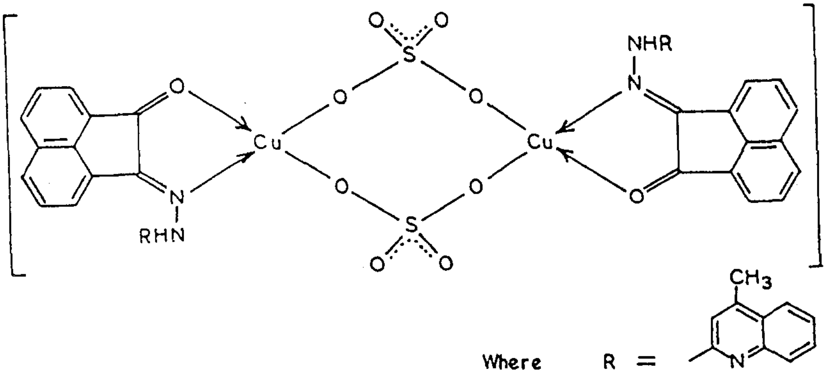

Fig. 3 [$CuLSO_4$]$_2$ (where *L* = AMH)

Table 5a Kinetic parameters from TG for copper(II) complexes

T/K	[CuLCl$_2$]			[CuLBr$_2$]			[CuLI$_2$]		
	X	Y	Z	X	Y	Z	X	Y	Z
523	0.029	1.910	7.35	–	–	–	–	–	–
542	–	–	–	–	–	–	0.12	1.845	6.72
553		–	–	–	–	–	0.18	1.808	6.55
558	–	–	–	–	–	–	0.30	1.792	6.42
563	0.058	1.776	7.10	–	–	–	–	–	–
568	–	–	–	–	–	–	0.36	1.760	6.22
573	–	–	–	0.16	1.745	6.64	–	–	–
578	0.088	1.730	6.92	–	–	–	0.48	1.730	6.07
588	–	–	–	–	–	–	0.60	1.700	5.93
593	0.117	1.686	6.81	0.25	1.686	6.44	–	–	–
598	–	–	–	–	–	–	0.72	1.672	5.81
603	0.147	1.658	6.72	0.33	1.658	6.32	–	–	–
613	0.176	1.630	6.65	–	–	–	–	–	–
618	–	–	–	0.44	1.618	6.18	–	–	–
623	0.200	1.600	6.60	–	–	–	–	–	–
633	0.220	1.579	6.57	0.55	1.579	6.06	–	–	–

where $X = \alpha$; $Y = 1/T \times 10^3$; $Z = -\log[-\log(1-\alpha)/T^2]$

Table 5b Kinetic parameters from TG for copper(II) complexes

T/K	$[CuL(OAc)_2]$			$[CuL(NO_3)_2]$			$[CuLSO_4]_2$		
	X	Y	Z	X	Y	Z	X	Y	Z
478	–	–	–	0.05	2.090	7.01	–	–	–
483	–	–	–	–	–	–	0.16	2.070	6.49
493	0.33	2.020	6.14	–	–	–	0.22	2.030	6.35
498	0.39	2.000	6.06	–	–	–	–	–	–
503	–	–	–	–	–	–	0.33	1.990	6.16
505	–	–	–	0.21	1.980	6.40	–	–	–
513	0.44	1.950	6.01	0.28	1.949	6.27	0.44	1.949	6.02
518	0.50	1.920	5.95	0.33	1.930	6.19	0.55	1.930	5.88
523	–	–	–	0.38	1.912	6.11	–	–	–
528	0.55	1.890	5.90	–	–	–	–	–	–
538	0.61	1.850	5.84	–	–	–	–	–	–

where $X = \alpha$; $Y = 1/T \times 10^3$; $Z = -\log[-\log(1-\alpha)/T^2]$

The relevant data needed for plotting linearization curves are recorded in Table 5a-5b and linearization plots are shown in Fig. 1a-f. The decomposition temperature, order of reaction and activation energy are presented in Table 6. The order of reaction in each case is found to be one.

Table 6 Thermal data for copper(II) complexes

Complex	TG		
	Temp. range /K	*n* / order of reaction	*E* /kcal·mol^{-1}
[$CuLCl_2$]	393–1202	1	10.98
[$CuLBr_2$]	422–1033	1	16.02
[$CuLI_2$]	513–953	1	25.62
[$CuL(OAc)_2$]	483–1193	1	21.96
[$CuL(NO_3)_2$]	473–1183	1	21.35
[$CuLSO_4$]$_2$	473–823	1	16.77

Thus, on the basis of above physico-chemical data in conjunction with consideration of ring strain, square planar structure (Fig. 2) seems to be likely for all the complexes except sulphato complex which seem to exist as dimer (Fig. 3).

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Zusammenfassung — Cu(II)-komplexe von Acenaphthoquinonmono(4-methylquinolinyl)-hydrazon (AMH) der allgemeinen Zusammensetzung [$CuLX_2$] (mit L = AMH; X = Cl, Br, I, OAc oder NO_3) (beim Sulfatokomplex lautet die Zusammensetzung [$CuLSO_4$]$_2$) wurden hergestellt und mittels Elementaranalyse, Messungen des magnetischen Momentes, Konduktivitätsmessungen, IR-, Elektronen- und EPR-Spektroskopie sowie mittels Thermoanalyse beschrieben. Für alle Komplexe wurde eine planare Geometrie nachgewiesen. Die TG-Kurven zeigen eine Zersetzung in einem Schritt, an dessen Ende die Bildung von Cu_2O steht.