

CADMIUM(II) COMPLEXES WITH AROYL HYDRAZONES

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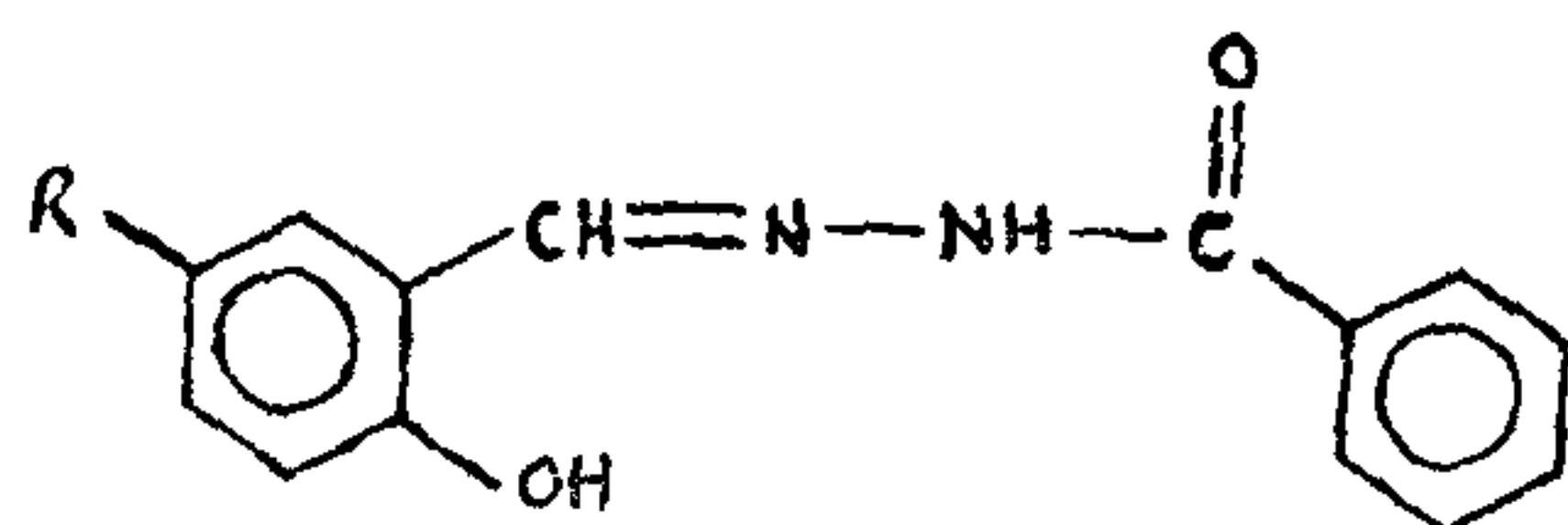
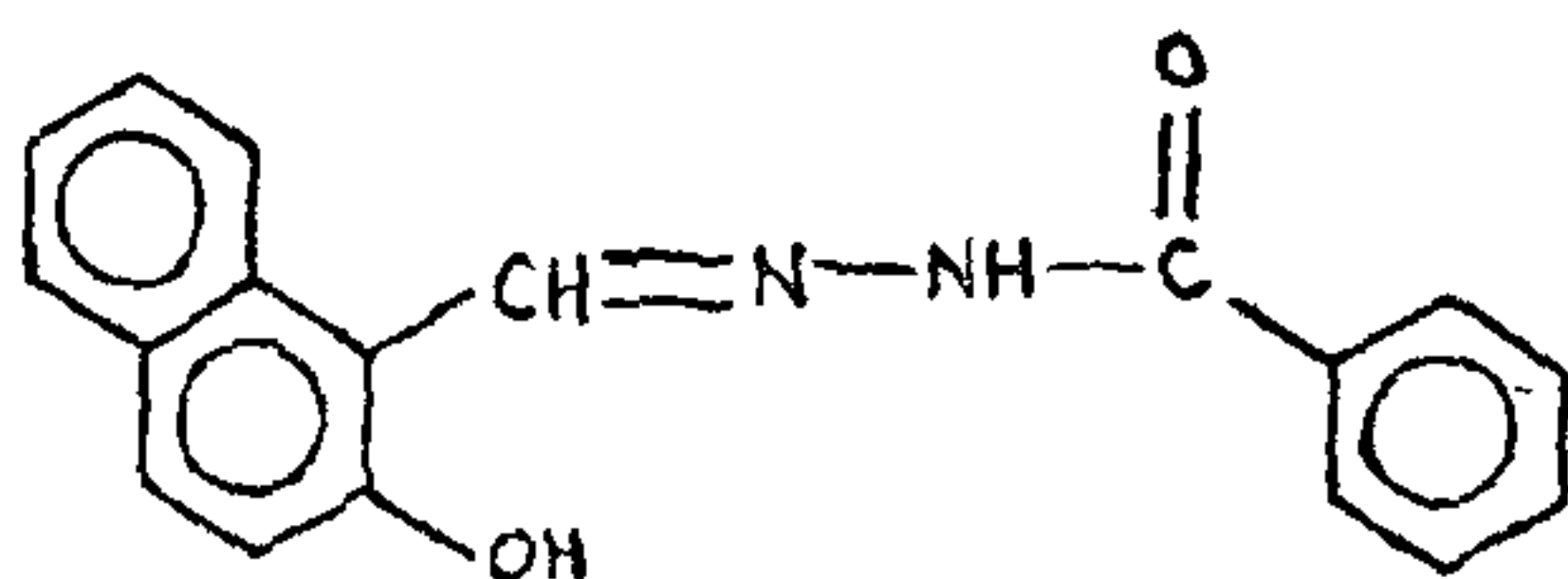
ABSTRACT

Eight complexes of Cd(II) have been prepared by reacting cadmium acetate with aroyl hydrazones in aqueous ethanolic medium. The elemental analyses indicate 1 : 2 stoichiometry. On the basis of infrared spectral studies, it has been shown that the ligands react in the *keto form* and the complexes have coordination number six.

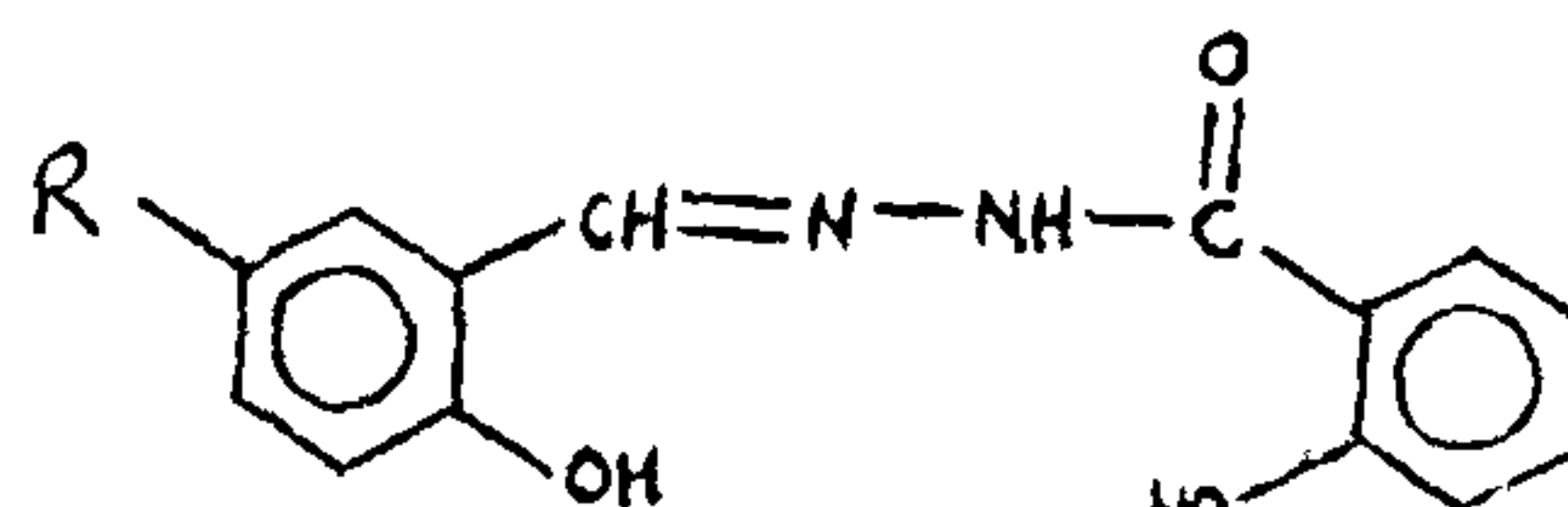
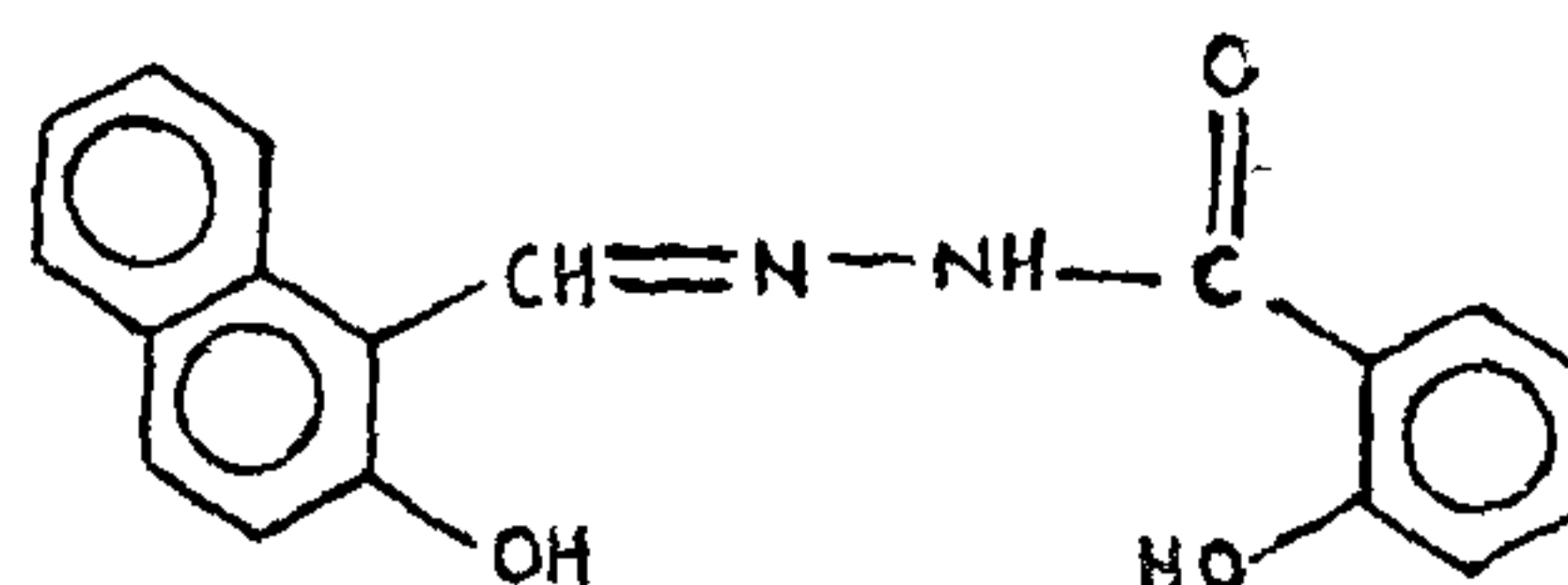
INTRODUCTION

THE hydrazides have been successfully tried for the complexation and they have been shown to coordinate through C=O and the terminal NH₂ groups¹. The hydrazones, containing C=O and C=N coordinating sites, are the reaction products of hydrazides and aldehydes or ketones². The *o*-hydroxy aldehydes or ketones yield the bases containing active -OH group in addition to the C=O and C=N coordinating groups. The earlier literature^{1,3} displays that these bases show monovalent bidentate behaviour. However, a few complexes with salicylhydrazone and isopropyl salicylhydrazone are reported in the literature, in which -OH group remains inert to the complex formation⁴. All this information stands as a testimony for the versatility of the hydrazones as chelating agents. However, the work on the complexes of divalent metal ions with hydrazones is limited.

The present work embodies the synthesis and spectral properties of Cd(II) complexes with the following hydrazones :

I
R=HII
R=CH₃III
R=Cl

IV

V
R=HVI
R=CH₃VII
R=Cl

VIII

EXPERIMENTAL

Materials and Method

Ethylbenzoate, methylsalicylate and hydrazine hydrate used for preparing the hydrazides were of reagent grade. Cadmium acetate was an analytical reagent. Benzoyl hydrazide and *o*-hydroxy-benzoylhydrazide were prepared according to standard methods⁵. The substituted aldehydes were prepared according to Duff's method⁶. The hydrazones were prepared by the reaction of benzoylhydrazide or *o*-hydroxy-benzoylhydrazide (0.1 M) with corresponding aldehyde (0.1 M) in ethanol.

Preparation of Complexes

To an ethanolic solution containing (0.2 M) of hydrazide and aldehyde, an aqueous cadmium acetate solution (0.1 M) was added. The reaction mixture was heated for a while on water bath and the complex precipitated was filtered and washed free from the ligand with ethanol and finally with ether and dried in vacuum over P₂O₅.

Elemental Analysis

Cadmium in the complexes was estimated gravimetrically as cadmium pyrophosphate⁷ and nitrogen

* For correspondence.

was estimated by Dumas method. The results of the elemental analysis are shown in Table I. 1600–1500 cm^{-1} are due to the aromatic C=C stretching vibrations.

TABLE I
Elemental analysis of Cd(II) complexes with aroyl hydrazones

Sl. No.	Ligand No.	Complex No.	Empirical formula	% Cd		% N	
				Found	Calcd.	Found	Calcd.
1.	I	IX	(C ₁₄ H ₁₁ N ₂ O ₂) ₂ Cd	19.77	19.03	10.11	9.48
2.	II	X	(C ₁₅ H ₁₃ N ₂ O ₂) ₂ Cd	17.50	18.18	9.10	9.06
3.	III	XI	(C ₁₄ H ₁₀ N ₂ O ₂ Cl) ₂ Cd	16.79	17.04	8.95	8.49
4.	IV	XII	(C ₁₈ H ₁₃ N ₂ O ₂) ₂ Cd	16.05	16.29	8.54	8.11
5.	V	XIII	(C ₁₄ H ₁₁ N ₂ O ₃) ₂ Cd	17.45	18.05	9.11	9.00
6.	VI	XIV	(C ₁₅ H ₁₃ N ₂ O ₃) ₂ Cd	17.66	17.28	8.92	8.61
7.	VII	XV	(C ₁₄ H ₁₀ N ₂ O ₃ Cl) ₂ Cd	16.80	16.26	7.89	8.10
8.	VIII	XVI	(C ₁₈ H ₁₃ N ₂ O ₃) ₂ Cd	16.10	15.56	7.35	7.75

Physical Measurements

The conductance measurements were done on an ELICO CM-82 conductivity bridge with a cell having cell constant 0.829 cm^{-1} . The IR spectra of the ligands and the complexes in nujol mull were recorded on Carlzeiss UR-10 recording spectrophotometer in the region of 4000–400 cm^{-1} .

RESULTS AND DISCUSSION

The complexes are yellow in colour, insoluble in common organic solvents. To some extent they are soluble in DMF and DMSO. The results of the elemental analysis (Table I) show that the complexes have 1 : 2 stoichiometry.

Conductance

The molar conductance in DMSO at the concentration $\sim 10^{-3}$ M is too small to measure. Hence the complexes are non-electrolytes in this solvent.

Infrared Spectra

The important infrared frequencies of the complexes are shown in Table II.

All the complexes show medium intensity broad band in the region 3225–3150 cm^{-1} due to NH stretch⁸. The complexes formed of the ligands I–IV, do not display any band in the region 2800–2700 cm^{-1} , whereas, the complexes of the ligands V–VIII have broad weak band around 2700 cm^{-1} characteristic of intramolecular H-bonded OH⁹. The bands of the ligands associated with the C=O and C=N stretching vibrations (Table II) show measurable shift towards low frequency in the complexes supporting the view that both C=O and C=N are involved in the coordinate bond formation. The three high intensity bands in the region

All the complexes show high frequency shift of the band around 1280 cm^{-1} attributable to the phenolic C–O stretch. In complexes XIII to XVI, there is a band around 1280 cm^{-1} having strong intensity. This is assigned to the phenolic C–O due to salicyloylhydrazide moiety.

These observations make us to envisage that the ligands I–VIII exist in the *keto form* in the complexes.

Of the several bands observed in the 600–400 cm^{-1} region which appear unchanged in the intensity and positions are due to the ligand skeletal vibrations. It is rather difficult to make the conclusive assignments amidst the high intensity skeletal bands which interfere with the M–N and M–O and M←O vibrations. Hence the assignments made here are based on the reported data and are tentative.

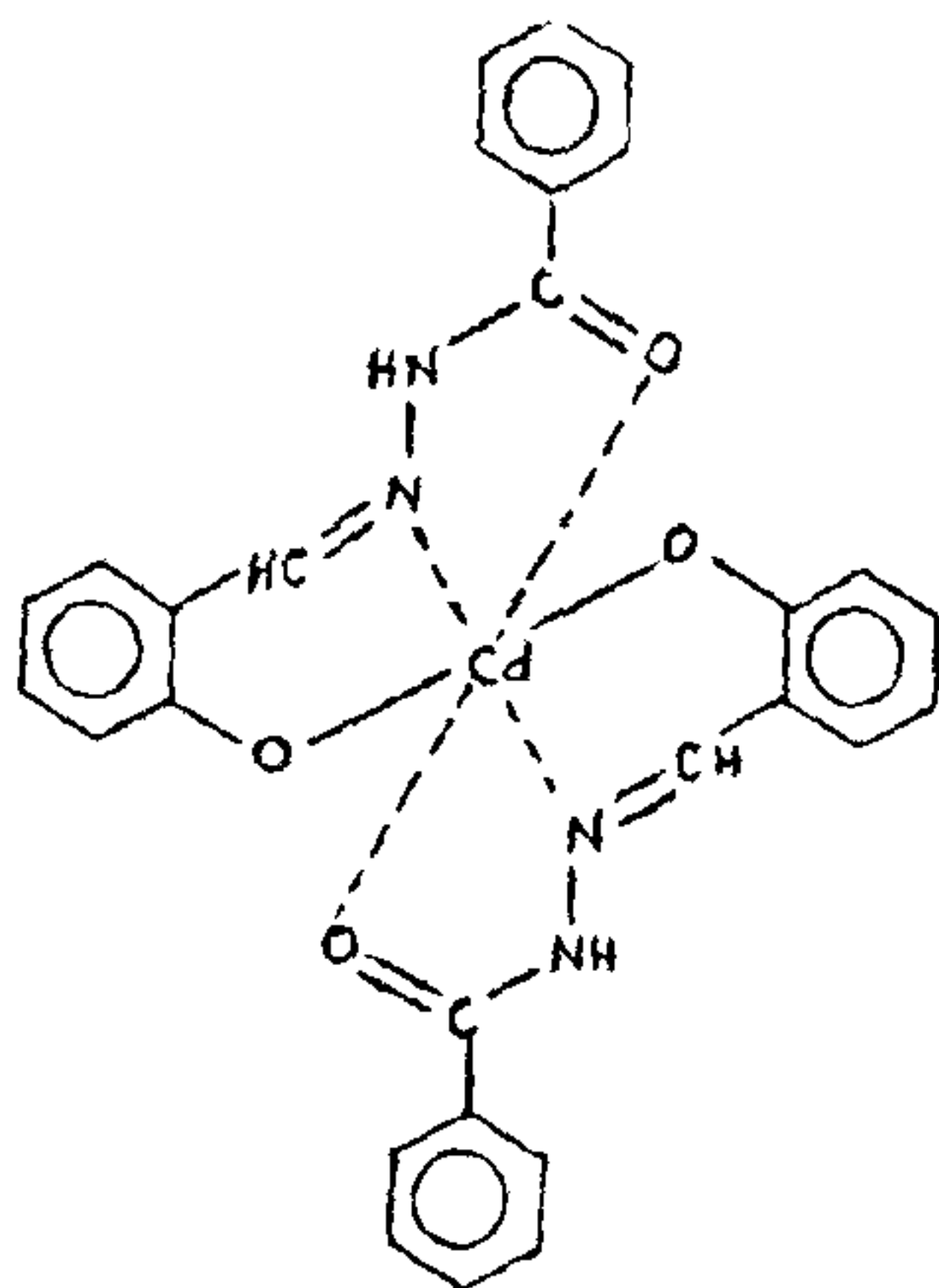
Amongst the three intense bands which appear in the 600–500 cm^{-1} region the band around 535 cm^{-1} is assigned to the Cd–N stretch as it shows little variation whereas the remaining bands are inert to the complexation. This assignment closely agrees with the previous assignments^{10,11}. The band observed in the region 490–460 cm^{-1} is an intense one and is assigned to the Cd–O band in view of the previous assignments¹. The band observed in the region 445–430 cm^{-1} , on analogy with the previous data^{11,12}, is assigned to the Cd–O stretch. All these bands show little variation in their positions indicating that all these complexes have the same coordination number.

On the basis of analytical data, infrared spectral results and the known hexacovalency of cadmium(II), the following structure may be proposed.

TABLE II
Important infrared frequencies (in cm^{-1}) of Cd(II) complexes with aroyl hydrazones and their assignments

Sl. No.	Ligand No.	Complex No.	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{O})$	$\nu(\text{Cd}-\text{N})$	$\frac{\nu(\text{C}'\leftarrow\text{O})}{\nu(\text{C}'\rightarrow\text{O})}$
1.	I	IX	3150 m	1625 s	1575 s	1575 s 1555 s 1500 m	1305 s	530 s	460 s 430 s
2.	II	X	3160 m	1630 s	1575 s	1575 s 1555 s 1500 w	1325 s	540 s	460 s 430 s
3.	III	XI	3150 m	1625 s	1580 s	1580 s 1545 s 1500 m	1325 s	535 s	465 s 430 s
4.	IV	XII	3160 m	1625 s	1585 s	1575 s 1560 s 1500 s	1325 s	530 s	470 s 445 s
5.	V	XIII	3220 m	1625 s	1580 s	1580 s 1565 s 1500 w	1340 s 1280 m	535 s	480 s 445 s
6.	VI	XIV	3150 m	1620 s	1575 s	1575 s 1555 w 1480 s	1280 s(br)	535 s	490 s 445 s
7.	VII	XV	3150 m	1625 s	1575 s	1575 s 1500 w	1335 s 1290 m	530 s	460 s —
8.	VIII	XVI	3225 m	1625 s	1585 s	1585 s 1565 s 1510 w	1320 m 1300 s	530 s	475 s 430 s

In the ligands the following assignments may be made: $\nu(\text{NH}) \sim 3200 \text{ cm}^{-1}$, $\nu(\text{intramolecular H-bonded OH}) 2800\text{--}2700 \text{ cm}^{-1}$, $\nu(\text{C}=\text{O}) 1670\text{--}1650 \text{ cm}^{-1}$, $\nu(\text{C}=\text{N}) 1625\text{--}1610 \text{ cm}^{-1}$ and $\nu(\text{C}-\text{O}) \sim 1280 \text{ cm}^{-1}$.



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