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Schiff Base Tetradentate Chelating Ligands and Cobalt Complexes from Acetylindanones

A. DRUSIANI, L. PLESSI, A. BIGOTTO, G. PELLIZER and G. COSTA

Istituto Chimico G. Ciamician, Università di Bologna, Bologna, Italy and Istituto Chimico, Università di Trieste, Trieste, Italy

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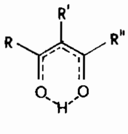
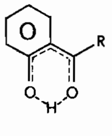
Model studies of reactive sites at coordinated metal atoms in biological systems involve the investigation of the effects of variation of structural characteristics in a series of suitably designed synthetic molecules reproducing the main features of biochemical reactivity. In this context the investigation of electronic and steric effects on reactions taking place in the coordination sphere of metals in complexes of polydentate ligand as models of prosthetic groups in metalloproteins is of current interest.

Metal chelates of Schiff bases have been studied for a long time as models of the most important classes of metabolites formed by chelates of tetrapyrrole macrocycles: porphyrins and corrins.

Most of the well known series of chelates of tetradentate Schiff base pseudomacrocycles with N_2O_2 donor atom set [1] are derived from the β diketones (A) or *o*-hydroxyarylketones (B) by condensation with diamines



A



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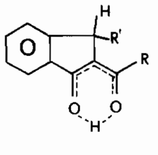


C

We report now the first examples of tetradentate Schiff bases derived from structure C where the β diketone is a 2-acylderivative of a saturated cyclic ketone. A similar arrangement is involved in previously studied Schiff base from formyl camphor and ethylenediamine but their metal chelates were not reported [2].

β Diketones

Acetylindanone (acin) was prepared after J. Thiele and K. Falk [3], 3-methyl- and 3-phenylindanone were obtained after Koelsch *et al.* [4].

2-acetyl, 3-methyl- and 3-phenylindanone were prepared *via* enamine from the parent ketone by extension of the method of Stork *et al.* [5].

2-acetyl- 3-methylindanone (macin)

Colourless crystals. M.p. 38 °C. $C_{12}H_{12}O_2$: C, 76.8 (76.57); H, 6.48 (6.42)%.

2-acetyl- 3-phenylindanone (phacin)

Colourless crystals. M.p. 135 °C. C, 80.9 (81.57); H, 5.55 (5.64)%.

The IR spectra in the 1700–1600 cm^{-1} region in KBr pellet can be clearly related to those of known β diketones: a strong band at 1660 cm^{-1} (acin), 1653 cm^{-1} (macin), 1655 cm^{-1} (phacin) is attributed to an essentially C–O stretching mode of the enolized form (Q_1 mode after Tayyari *et al.* [6]; a strong doublet at 1619–1605 cm^{-1} (acin), 1615(sh)–1606 (macin) and an unresolved peak at 1606 cm^{-1} (phacin) are assigned to the enolised β diketone C=C stretching mode (Q_2) and to a phenyl ring skeletal stretching. IR spectra in $CHCl_3$ show for acin and macin the unenolized ketonic absorption band at 1701 and 1704 cm^{-1} respectively. This absorption is much weaker (as a shoulder) in the phacin solution.

The 60 MHz proton NMR spectrum in $CDCl_3$ confirms the keton-enol structure which is revealed by the 13.5 δ (ppm from TMS) in the acin, 12.7 δ in macin and 12.15 in phacin for the hydrogen bonded proton.

The aromatic protons signals are observed between 6.9 and 8.0 δ in all above compounds. The signal at 3.5 δ is attributed to the cycloaliphatic ring protons in the enolic form of acin while the proton in 3 position of macin resonates as a quartet (J = 7 Hz) centered at 3.75 δ and that of phacin resonated as a slightly broadened singlet at 4.85. The peaks at 2.5 and 2.15 δ in acin, 2.45 and 2.2 δ in macin and 2.4 and 1.8 δ in phacin are assigned to the acetyl-CH_3 group in the β diketone and keto-enol forms respectively. The ring-CH_3 group of macin gives a doublet at 1.4 δ (J = 7 Hz). The integrated intensities of the acetyl-CH_3 group peaks at 2.5, 2.45 and 2.4 of the ketonic form as compared with those of the enolic form at 2.15, 2.2 and 1.8 respectively indicate that the keto-enol structure is predominant (80–90%).

In agreement with a previous report [7] the β diketone form of the acin gives rise to an ABX pattern for the resonances of the C-3 and C-2 protons in the cycloaliphatic ring. In the case of macin the C-2 proton appears as a doublet ($^3J_{HH}$ = 4 Hz at 3.5 δ. In the case of phacin it appears as a doublet ($^3J_{HH}$ = 4 Hz centered at 3.8 δ and the C-3 proton gives rise to a broad doublet (J = 4 Hz) centered at 5.05 δ.

IR and nmr spectra do not allow one to draw conclusions about the structure of the enolic form [8]. The predominant form is expected to be that involving the exocyclic double bond, as that involving the endocyclic double bond is thought to be unfavoured owing to the ring strain in the five membered cycle as in β formylcamphor [9] formylcycloalkanones [10] and 2-acetylcyclopentanone [11, 12].

Schiff bases

Schiff bases of acin and macin were obtained with standard methods [13] from the β diketones and ethylenediamine in boiling methanol.

N,N'-ethylenebis(2-acetylindanone imine) (acinen)

Two forms were obtained from methanol: yellow needles and brown crystals. M.p. 215 °C. $C_{24}H_{24}N_2O_2$: C, 77.0 (77.39); H, 6.49 (6.47); N 7.52 (7.53)%.

N,N'-ethylenebis(3-methyl-2-acetylindanoneimine) (macinen)

Yellow crystals from methanol. M.p. 214 °C. $C_{26}H_{28}N_2O_2$: C, 78.5 (77.96); H, 6.81 (7.04); N 6.88 (6.99)%.

Attempts to prepare the Schiff base from 3-phenyl-2-acetyl indanone and ethylenediamine were unsuccessful.

The IR spectra of the Schiff base *acinen* (both the yellow and the brown crystals) and *macinen* show the disappearance of the C–O stretching found in the parent β diketones at 1660 and 1653 cm^{-1} respectively while a bond near 1620 cm^{-1} is still present. Absorptions in this region are found as follows: in acinen (yellow and brown crystals) as an unresolved band at 1578 cm^{-1}; in macinen as a band at 1595 with two shoulders at 1584 and 1558 cm^{-1}. This compares well with the absorption pattern reported for the majority of condensation products of β diketones with diamines [14].

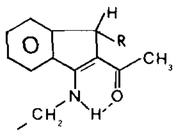
The yellow and the brown crystals of acinen in KBr pellet give IR spectra with a different absorption pattern in the 3500–3300 cm^{-1} region, and some minor differences also in the 1500–700 cm^{-1} region. In the yellow form two sharp bands are found at 3560 and 3485 cm^{-1} while the brown form shows only one band at 3360 cm^{-1} superimposed to a broad absorption centered at 3300 cm^{-1}. The pattern of IR bands in the diagnostic region is in agreement with the presence of an appreciable amount of the ketoamine structure [14].

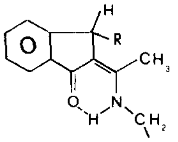
The proton NMR spectra of acinen and macinen clearly show the signals due to the hydrogen bonded proton at about 11 δ and to the aromatic ring protons at 7.3–7.8 δ.

Both the yellow and brown forms of acinen show in $CDCl_3$ solution the peak at 3.4 δ due to the cycloaliphatic ring protons while the signals centered at 3.5 δ are attributed to the ethylene bridge and the CH_3 resonance is found at 2.1 δ.

In the macinen spectrum the C-3 proton and both the CH_3 groups give rise to a pattern more complicated than expected, and furthermore the methyl resonance changes slowly with time after dissolution in $CDCl_3$. Only the low field peaks of the C-3 proton quartets are visible allowing the assignment of 3.7 δ (J = 7 Hz), while the ethylene bridge protons resonate in the range 3.5–3.6. Two ring CH_3 signals appear as doublets at δ = 1.25 and 1.35 (J = 7 Hz in freshly prepared solutions). The other CH_3 also gives rise to two peaks at 2.1 and 2.15 δ. This behaviour suggests the presence of more than one isomeric species in solution.

On the other hand the positions of the main proton resonances compare well with the data reported for acacen and related Schiff bases which are assumed to be in the ketoenamine structure (I–II).





If the assumptions about the relative stability of the *endo*- and *exo*-cyclic double bonds are valid also for the Schiff bases, structure II is to be preferred owing to the lesser strain.

Cobalt chelates

The cobalt complexes were prepared from the Schiff bases by addition of $Co(CH_3COO)_2 \cdot 4H_2O$ in water-methanol solution under inert gas atmosphere. From both acinen and macinen the cobalt chelates were obtained as bright-red crystals.

N,N'-ethylenebis (2-acetylindanone iminato) cobalt (II) (Co acinen)

$C_{24}H_{23}N_2O_2Co$: C, 67.5 (67.13); H, 5.23 (5.16); N, 6.42 (6.52)%.

N,N'-ethylenebis (3-methyl-2-acetylindanone iminato) cobalt(II) (Co macinen)

$C_{26}H_{27}N_2O_2Co$: C, 67.7 (68.3); H, 5.66 (5.7); N 5.78 (6.1)%.

The IR spectra of Co-acinen and Co-macinen show the disappearance of the strong band of Schiff bases at 1620 cm^{-1}.

The other bands at 1607, 1585 and 1550 cm^{-1} in *Co-acinen* and at 1609, 1590, 1545 cm^{-1} in the Co-macinen remain practically unshifted relative to the parent Schiff base. This behaviour is at variance with that of Co-salen but compares well with that of Co-acacen and related chelates of ketoamines [15] which show in this range the low frequency bands attributed to the C=C stretching and to the perturbed carbonyl in the chelate.

The redox properties and reactivity of the present chelates are being studied in the aprotic solvents used for the cobalt complexes of the salen and acacen series.

In dimethylformamide–0.1 *M* $LiClO_4$ both Co-acinen and Co-macinen undergo a one electron oxidation at half wave potential ($E\frac{1}{2}$) = –0.46 and –0.47 *vs.* SCE, respectively. A reversible one electron reduction occurs at $E\frac{1}{2}$ = –1.44 and –1.47 *vs.* SCE, respectively.

The influence of the CH_3 group as substituent at C-3 in the five membered ring is apparently very limited as far as the redox behaviour is concerned.

On the other hand the comparison of $E\frac{1}{2}$(ox) and E (red) with those of Co salen and Co acacen series shows that in the present chelates the oxidation and the reduction takes place at intermediate potentials between those of Co(salen) and Co(acacen).

Preliminary experiments indicate that both the present chelates behave as oxygen carriers in the Co(II) oxidation state.

The controlled potential reduction at –1.5 *vs.* SCE in DMF gives a deep green solution which apparently contains the Co(I) species. The reactivity of the present Co(I) chelates, which appears to be qualitatively similar to that of the Co(I) salen and related chelates is being investigated.

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