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Synthesis and Characterization of a Series of New Mixed Ligand Complexes of Manganese(III), Iron(III), Nickel(II), Copper(II) and Zinc(II) with Schiff Bases of N,N-diethylamino-dithiocarbamate as Ligands

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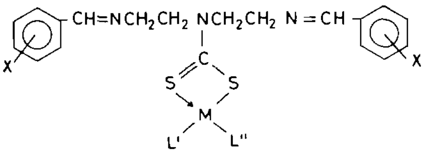
Abstract

Twenty new bioactive complexes of Mn(III), Fe(III), Ni(II), Cu(II) and Zn(II) have been prepared containing Schiff bases of N,N-diethylaminodithiocarbamate as ligands. These complexes have been characterized by elemental analyses, IR and UV-Vis spectroscopy as well as by magnetic susceptibility measurements. The spectra of the complexes suggest that the ligands are coordinated to the metal ions via the sulfur atoms of the dithiocarbamato group.

Introduction

Continuing our theoretical and practical interest in the synthesis and study of new dithiocarbamato complexes [1], this paper reports on the formation and study of a series of twenty mixed-ligand complexes of some transition metal ions with the Schiff bases of N,N-diethylaminodithiocarbamate.

The general formulae of the complexes in question are illustrated in Scheme 1.



where X = H, *o*-Cl, *m*-Cl, *p*-Cl,
and M = Mn(III), L′ = S_2CNH_2, L″ = OH
or M = Fe(III), L′ = S_2CNH_2, L″ = Cl
or M = Ni(II), Cu(II), Zn(II), L′ = S_2CNH_2.
(for the Ni(II), Cu(II) and Zn(II) the L″ is absent).

Scheme 1.

The idea of synthesizing complexes having more pronounced antifungal and antibacterial activities was the objective of this work. Consequently, we tried to enhance the very well-known biological action of the dithiocarbamate ligand [2] by attaching in it a chlorophenyl group, which may increase the activity of this ligand [3] and its complexes.

Another reason for the synthesis of these complexes was the fact that these types of ligands have many potential donor sites. Hence, the reaction of the above ligands with several metal ions may lead to the preparation of binuclear complexes with more advantages, considering that the very well-known commercial product 'zincomaneb', $ZnMn(S_2CHNCH_2CH_2NHCS_2)_x$, combines successfully with the bioactivity of zineb, $Zn(S_2CHNCH_2CH_2NHCS_2)_x$, and maneb $Mn(S_2CHNCH_2CH_2NHCS_2)_x$.

As far as we know, the Schiff bases of the N,N-diethylaminodithiocarbamates comprise a new series of ligands, since some simple bases with diethylenetriamine (dien) have already been used as ligands [4].

Calabro and Burmeister [5] have prepared related mixed-ligand complexes of the formula $[(C_2H_5)_2NCH_2CH_2]_2NCS_2Au(SCN)_2$ and have come to the conclusion that the ambidentate mode of the thiocyanate can possibly exist in the same complex.

Also, McCormick *et al.* [6] have already studied several dithiocarbamates cationic complexes of dien derivatives.

Experimental

Preparation of the Compounds

Schiff bases have been prepared either by mixing 0.01 mol diethylenetriamine (dien) directly with 0.02 mol of an aldehyde or by mixing the above reagents in methanol.

The general method of preparation was as follows. To a stirred solution of the appropriate aldehyde (0.02 mol) in 40 ml methanol, 0.01 mol of diethylenetriamine dissolved in 40 ml methanol was added. The solution was refluxed for 1 h and cooled to room temperature. Then, 0.03 mol of ammonia solution and 0.02 mol of carbon disulfide were added. The ligands were not isolated but complexed directly to the metal ions which were added as methanolic

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solutions of metal chlorides. The compounds which precipitated immediately were filtered and washed several times with methanol and ether and were dried overnight *in vacuo*, over $CaCl_2$.

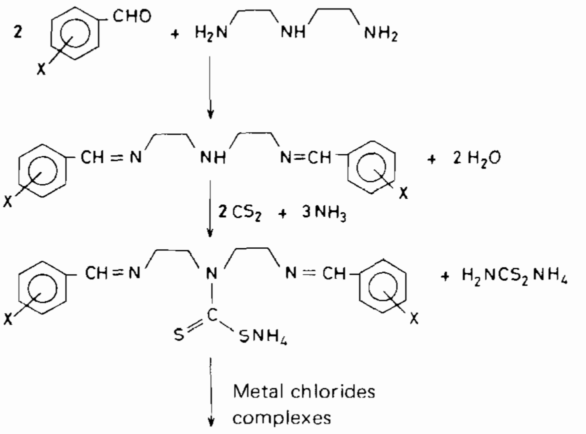
In the case of manganese complexes, due to the instability of manganese(II) in air, all operations were carried out under nitrogen. In this case, after mixing the appropriate quantities of the reagents, a yellow precipitate was formed immediately which was removed by filtration and was then washed with methanol and ether. The compound easily oxidized in air into the brown Mn(III) complexes. Therefore, the experiments were carried out on this brown product which is stable for long periods.

Measurements

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 B elemental analyser. Sulfur and metals analyses were carried out by standard [7] techniques. The chlorine was determined by Volhard's method. The IR spectra of all compounds were measured from 4000 to 200 cm^{-1}, on a Perkin-Elmer 467 spectrophotometer using KBr discs. Electronic absorption spectra were recorded on a Perkin-Elmer/Hitachi 200 spectrophotometer, using freshly prepared DMF or DMSO solutions. Magnetic susceptibility measurements, at room temperature, were carried out using the Faraday technique and calibration using $Hg[Co(SCN)_4]$. All measurements were corrected for diamagnetism by using Pascal's constants.

Results and Discussion

The Shiff bases of diethylenetriamine (dien) with benzaldehyde or its derivatives were prepared and their reaction with CS_2 was followed to produce dithiocarbamato ligands from the secondary amino group. It was not possible to isolate these compounds, therefore, they were used *in situ* for the preparation of the complexes with transition metal ions according to the following credible general chemical eqns.:



According to the elemental analyses the prepared complexes are formulated as shown in Table I. All complexes are soluble in DMSO and DMF, slightly soluble in $CHCl_3$ but insoluble in common organic solvents. An insight into the chemical bonding and structure of the complexes was gained by studying their IR and electronic spectral data, as well as from the measurements of their magnetic moments.

The infrared spectra of all complexes displayed a strong absorption band in the region of 1640–1660 cm^{-1} which was assigned to the C=N stretching mode of the Schiff bases [8]. Considering that the free ligands exhibit this band in the same region, we can conclude that the imine nitrogen donor atoms were not involved in the coordination.

The very strong band at *ca.* 1500 cm^{-1} was attributed [9] to the stretching vibration of the partially double bond character of the carbon–nitrogen bond ($C\underline{\cdots}N$) of the coordinated dithiocarbamate ligand. Another strong band about 1440 cm^{-1}, was also attributed to the stretching vibration of the $C\underline{\cdots}N$ bond of the dithiocarbamato group of ammonia (L′, Scheme 1). This band has also been observed by previous authors in the spectra of complexes of the general type $(H_2NCS_2)_2M$ [10].

The bands in the region of 950–1050 cm^{-1} were attributed to the stretching mode of the C–S bond. The position of this band was used by several authors [11] as a criterion for symmetric or asymmetric coordination of the dithiocarbamato group. The band at about 970 cm^{-1} in the IR of nickel complexes suggests isobidentate linking of the dithiocarbamato group. In the IR spectra of copper, manganese and iron complexes the $\nu(C\underline{\cdots}S)$ band occurs in the region of 950–995 cm^{-1} either as a single broad band of low intensity or evincing splitting. Both the broadening and splitting of this band indicates the anisobidentate linking of the dithiocarbamate ligands. In the case of zinc complexes, these bands were broader and stronger than the corresponding ones of the other complexes. The large broadening of this band may be due to the uniequivalent bonding of dithiocarbamato group, as well as to the interaction between the zinc atom and a sulfur atom of a neighbouring molecule in the crystal unit. This phenomenon is very common among zinc dithiocarbamato complexes [12].

The low intensity bands in the region 350–400 cm^{-1} were attributed to the M–S stretching vibration thus confirming the formation of the complexes [13–15]. In the spectra of Fe(III) compounds the ν(Fe–S) bands are weak and also show splitting. This probably reflects on the coexistence of low and high spin complexes of iron [16]. Furthermore, there is another band at 320 cm^{-1} which is due to the stretching mode of Fe–Cl bond [17].

TABLE I. Analytical Data[a], Melting Points (°C), Yield, Colour and Relevant IR Frequencies (cm^{-1}) of the New N,N-diethylaminodithiocarbamato Complexes of Mn(III), Fe(III), Ni(II), Cu(II) and Zn(II), with their Assignements.

Compound	% C	% H	% N	% S	% M	M.P.[c]	Yield (%)	Colour	$\nu(C{\cdots}N)^b$	$\nu(C{\cdots}S)^b$	$(M-S)^b$
$[C_6H_5CH{=}NCH_2CH_2]_2NCS_2Mn(OH)(S_2CNH_2)$	46.22 (46.33)	4.49 (4.44)	10.94 (10.81)	24.64 (24.71)	10.51 (10.61)	75	58	brown	1490s 1430vs	980w 965w	360w–br
$[C_6H_5CH{=}NCH_2CH_2]_2NCS_2Fe(Cl)(S_2CNH_2)$	44.85 (44.65)	4.21 (4.09)	10.58 (10.41)	23.96 (23.81)	10.15 (10.42)	84	65	black	1510vs 1460vs	970w	365w
$[C_6H_5CH{=}NCH_2CH_2]_2NCS_2Ni(S_2CNH_2)$	47.45 (47.55)	4.32 (4.36)	10.93 (11.09)	25.55 (25.36)	11.51 (11.63)	125	32	yellow green	1490vs 1450s	965w	380m
$[C_6H_5CH{=}NCH_2CH_2]_2NCS_2Cu(S_2CNH_2)$	47.04 (47.10)	4.42 (4.32)	10.90 (10.99)	25.18 (25.12)	12.38 (12.47)	112	80	brown	1500vs 1430s	980w	360w–br
$[C_6H_5CH{=}NCH_2CH_2]_2NCS_2Zn(S_2CNH_2)$	46.89 (46.93)	4.45 (4.30)	11.01 (10.95)	24.92 (25.03)	13.00 (12.78)	110	40	yellowish	1490s 1450vs	990m 970w	375w–br
$[o\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Mn(OH)(S_2CNH_2)$	40.67 (40.88)	3.69 (3.57)	9.21 (9.54)	21.78 (21.80)	9.30 (9.36)	103	48	brown	1475s 1435vs	985w 960w	370w
$[o\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Fe(Cl)(S_2CNH_2)$	39.44 (39.57)	3.53 (3.30)	8.98 (9.23)	21.25 (21.10)	9.56 (9.23)	129	66	black	1480s 1450vs	985w 965w	355w
$[o\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Ni(S_2CNH_2)$	41.82 (41.83)	3.65 (3.49)	10.04 (9.76)	22.13 (22.31)	10.15 (10.23)	140	60	yellow green	1502vs 1450s	965w	380m
$[o\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Cu(S_2CNH_2)$	41.05 (41.48)	3.60 (3.46)	9.60 (9.68)	21.98 (22.12)	11.04 (10.98)	138	70	brown	1510vs 1440vs	975w	352w
$[o\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Zn(S_2CNH_2)$	41.06 (41.35)	3.40 (3.44)	9.85 (9.65)	21.95 (22.05)	11.32 (11.26)	130	74	yellowish	1480s 1445vs	990m 965m	375w
$[m\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Mn(OH)(S_2CNH_2)$	41.05 (40.88)	3.61 (3.57)	9.76 (9.54)	22.10 (21.80)	9.50 (9.36)	95	63	brown	1480vs 1430vs	980w	375w
$[m\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Fe(Cl)(S_2CNH_2)$	39.80 (39.57)	3.42 (3.30)	9.37 (9.23)	21.35 (21.10)	9.00 (9.23)	115	55	black	1470s 1450vs	980w	360w
$[m\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Ni(S_2CNH_2)$	42.00 (41.83)	3.54 (3.49)	9.95 (9.76)	22.57 (22.31)	10.30 (10.23)	88	72	yellow green	1485vs 1455vs	960w	385m
$[m\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Cu(S_2CNH_2)$	41.65 (41.48)	3.48 (3.46)	9.80 (9.68)	22.35 (22.12)	10.60 (10.98)	105	60	brown	1480vs 1450vs	970w–br	355w
$[m\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Zn(S_2CNH_2)$	41.80 (41.35)	3.50 (3.44)	9.80 (9.65)	21.79 (22.05)	11.32 (11.26)	102	65	yellowish	1480vs 1430vs	990m 965m	375w
$[p\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Mn(OH)(S_2CNH_2)$	40.60 (40.88)	3.40 (3.57)	9.81 (9.54)	21.57 (21.80)	9.25 (9.36)	65	60	brown	1500vs 1440vs	970w	375w

(continued overleaf)

TABLE I *(continued)*

Compound	% C	% H	% N	% S	% M	M.P.^{c}	Yield (%)	Colour	$\nu(C\cdots N)^b$	$\nu(C\cdots S)^b$	$(M-S)^b$
$[p\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Fe(Cl)(S_2CNH_2)$	39.87 (39.57)	3.32 (3.30)	9.33 (9.23)	21.27 (21.10)	9.35 (9.23)	113	45	black	1500vs 1455vs	970w	355w
$[p\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Ni(S_2CNH_2)$	41.60 (41.83)	3.40 (3.49)	9.90 (9.76)	22.54 (22.31)	10.10 (10.23)	178	37	yellow green	1500vs 1465s	965w	382m
$[p\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Cu(S_2CNH_2)$	41.60 (41.48)	3.50 (3.46)	9.92 (9.68)	22.40 (22.12)	10.62 (10.98)	145	78	brown	1500vs 1430s	970w	355w
$[p\text{-}ClC_6H_4CH{=}NCH_2CH_2]_2NCS_2Zn(S_2CNH_2)$	41.00 (41.35)	3.35 (3.44)	9.70 (9.65)	21.85 (22.05)	11.00 (11.26)	137	38	yellowish	1500vs 1440vs	990m 970m	375w

[a] Figures in parentheses are the calculated values. [b] vs = very strong, s = strong, m = medium, w = weak, br = broad. [c] Decomposition.

In the IR spectra of the manganese(III) complexes the most striking feature is the appearance of a medium intensity band at 3500 cm^{-1} which is assigned as ν(O–H) of a coordinated hydroxide group [18].

The insight into the structure of the complexes was further supported by the electronic spectral data in Table II. Bands I and II, at *ca.* 260 and 290 nm were assigned [9] to the intraligand $\pi^* \leftarrow \pi$ transitions mainly located on the N–C=S and S–C=S groups, respectively, while band **III** at *ca.* 350 nm is due to a transition of the type $\pi^* \leftarrow n$ located on the sulfur atom.

Generally, in the complexes studied, band I appears almost at the same position (*ca.* 260 nm) for all complexes while bands II and III were found at different positions with different shapes depending on the nature of the complex. In some cases band III was not observed and possibly is obscured by charge transfer bands.

In the electronic spectra of zinc complexes the presence of high intensity intraligand [23, 24] band II at 290 nm confirms [12, 20] the anisobidentate linking of the dithiocarbamato group as inferred from the IR spectral data of the complexes.

Band II in the spectra of Cu(II) complexes appeared as a shoulder on band I (265 nm), again showing the anisobidentate coordination of the dithiocarbamato group. The shoulder at 510 nm (band IV) and band V at 630 nm is evidence of a square planar geometry around the metal [21, 22]. In the spectra of nickel complexes the bands at 430 and 480 nm (bands IV and V) are also characteristic of a square planar arrangement [23, 24]. This structure is further supported by the absence of band II suggesting the isobidentate linking of the ligands (coordination number four) [19]. Finally, the band at 630 nm with a low absorption coefficient is a crystal field band. In the electronic spectra of Fe(III) complexes the strong bands at 350, 500, and 600 nm were assigned as charge transfer bands of the eg $\leftarrow \pi$, $\pi^* \leftarrow$ eg and $\pi^* \leftarrow t_{2g}$ type, respectively, in agreement with the conclusions of Pasek [25], Nikolov [26], Tsipis [27] *et al.* who studied related iron(III) systems. The electronic spectra of the iron(III) complexes in freshly prepared DMF solutions are almost similar to those in other solvents but are changed when kept in the solutions for long periods. It is possible, in this case, that a molecule of a solvent is coordinated directly to the metal atom, as a sixth donor $[Fe(dtc)_2Cl(DMF)]$ or the solvent leads to a binuclear complex after dimerization $[Fe_2(dtc)_4Cl_2]$. In both cases, the geometry should be octahedral. In the electronic spectra of manganese complexes, in chloroform solutions, the band at 265 nm (band I) and the shoulder at *ca.* 300 nm (band II) justify the almost bidentate linking of the dithiocarbamato group. The charge transfer band III

TABLE II. Electronic Spectra and Magnetic Data of the New N,N-diethylamino-dithiocarbamato Complexes of Mn(III), Fe(III), Ni(II), Cu(II) and Zn(II).

Compound	Band I	Band II	Band III	Band IV	Band V	Band VI	μ_{eff} (BM)
$(C_6H_5CH{=}NCH_2CH_2)_2NCS_2Fe(Cl)(S_2CNH_2)$	267[a](4.44)[b]	290sh[c]	352(3.59)	515sh	630(2.84)		4.92
$(o\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Fe(Cl)(S_2CNH_2)$	261(4.70)	300sh	361(3.69)	515(3.24)	606(3.16)		4.72
$(m\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Fe(Cl)(S_2CNH_2)$	262(4.65)	290sh	350(3.63)	510(3.18)	610(3.05)		4.93
$(p\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Fe(Cl)(S_2CNH_2)$	265(4.77)	292sh	355(3.75)	507(3.15)	600(3.16)		4.61
$(C_6H_5CH{=}NCH_2CH_2)_2NCS_2Mn(OH)(S_2CNH_2)$	265(4.45)	280sh	494(2.90)	600sh			4.64
$(o\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Mn(OH)(S_2CNH_2)$	267(4.46)	301sh	495(2.97)	645sh			4.70
$(m\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Mn(OH)(S_2CNH)$	266(4.48)	295sh	490(2.95)	620sh			4.80
$(p\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Mn(OH)(S_2CNH_2)$	265(4.56)	302sh	495(2.95)	600sh			4.61
$(C_6H_5CH{=}NCH_2CH_2)_2NCS_2Ni(S_2CNH_2)$	262(4.58)	325(4.58)	385(3.70)	435(3.14)	475(2.31)	625(2.00)	dia.
$(o\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Ni(S_2CNH_2)$	265(4.06)	327(4.48)	388(3.71)	430(3.11)	492(2.36)	633(2.06)	dia.
$(m\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Ni(S_2CNH_2)$	265(4.30)	325(4.51)	386(3.70)	429(3.15)	490(2.35)	630(2.01)	dia.
$(p\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Ni(S_2CNH_2)$	264(4.60)	325(4.66)	388(3.83)	435(3.30)	490(2.49)	640(2.17)	dia.
$(C_6H_5CH{=}NCH_2CH_2)_2NCS_2Cu(S_2CNH_2)$	265(4.37)	290sh	435(3.69)	505sh	630(2.84)		0.92
$(o\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Cu(S_2CNH_2)$	266(4.37)	291sh	436(3.64)	507sh	633(2.71)		1.03
$(m\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Cu(S_2CNH_2)$	265(4.35)	290sh	435(3.63)	510sh	631(2.39)		1.49
$(p\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Cu(S_2CNH_2)$	265(4.53)	292sh	435(3.61)	510sh	633(2.41)		1.20
$(C_6H_5CH{=}NCH_2CH_2)_2NCS_2Zn(S_2CNH_2)$	258(4.35)	302(4.44)					dia.
$(o\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Zn(S_2CNH_2)$	267(4.51)	280(4.39)					dia.
$(m\text{-}ClC_6H_4CH{=}NCH_2CH_2)_2NCS_2Zn(S_2CNH_2)$	265(4.35)	290(4.45)					dia.
$(p\text{-}ClO_6H_4CH{=}NCH_2CH_2)_2NCS_2Zn(S_2CNH_2)$	266(4.46)	297(4.30)					dia.

[a] λ/nm. [b] $\log \epsilon_{mol}$. [c] sh = shoulder.

(350 nm) [28] is more evident in $CHCl_3$ solutions and disappeared in DMF solutions whereas the shoulder at 290 nm appears as a separated band. This phenomenon may be attributed to the coordination tendency of the DMF which results in changing the mode of linking the dithiocarbamato group from bidentate to monodentate. The band at 500 nm and the shoulder at 600 nm strongly suggest the octahedral geometry [29–31]. These bands are found in the same position in both solvents ($CHCl_3$ and DMF).

Table II lists the magnetic data, at room temperature, of all the complexes studied. The μ_{eff} of Cu(II) complexes are lower than 1.73 BM which is consistent with an orbitally degenerate ground state. However, the low μ_{eff} values provide indications for magnetic exchange interactions either inter or intramolecular [32, 33]. The dithiocarbamates of nickel are diamagnetic as might be expected for low-spin d^8 complexes of square planar geometry [34].

The μ_{eff} values for the Fe(III) complexes are consistent with a square pyramidal configuration with an $S = 3/2$ ground state [17, 35]. Finally, the calculated μ_{eff} values of the manganese complexes closely resembled those found for high spin d^4 systems indicating the presence of Mn(III), in a typical octahedral environment [4, 8]. This provides an additional indication of the oxidation of the Mn(II) complexes during the preparation [36]. The octahedral geometry is justified by dimerization through a bridging of two hydroxyl groups [37] in agreement with the IR spectral data.

Bioactivity

The antibacterial and antifungal efficiency of prepared dithiocarbamato complexes was studied against *Staphylococus SPP*, *Pasteurella multocida*, *Eschericia coli*, *Bacilus cereus* and *Candida albicans* using a culture media Mueller–Hinton agar.

The results of the biological test showed that the paramagnetic complexes of Mn(III), Fe(III) and Cu(II) are more active than the diamagnetic complexes of Ni(II) and Zn(II). The comparison of the biological activity of *o*-chloro substituted in the aromatic ring compounds to those of the corresponding *m*-, *p*- and non substituted derivatives shows that the *o*-derivatives are more active than the others.

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